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$SrBi_2Ta_2O_9$ ferroelectric thick films prepared by electrophoretic deposition using aqueous suspension

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Abstract

$SrBi_2Ta_2O_9$ ferroelectric thick films were prepared by electrophoretic deposition (EPD). For that, ceramic powders were prepared by chemical method in order to obtain compounds with chemical homogeneity. The polymeric precursor method was used for the synthesis of the $SrBi_2Ta_2O_9$ powder. The crystallographic structure of the powder was examined by X-ray diffraction, and the surface area was determined by single point BET adsorption. The 0.03 vol.% suspension was formed by dispersing the powder in water using two different polymers as dispersants: an ester polyphosphate (C213) and an ammonium polyacrilate (Darvan 821-A). It was investigated the influence of the different dispersants in the surface properties of the powder by zeta potential measurements. The films were deposited on platinum-coated alumina and $Pt/Ti/SiO_2/Si$ substrates by a 4 mA constant current, for 10 min, using two parallel electrodes placed at a separation distance of 3 mm in the suspension. Several cycles of deposition-drying of the deposit were carried out until reaching the desired thickness. After thermal treatment at temperatures ranging from 700 to 1000 °C, the films were characterized by X-ray diffraction and scanning electron microscopy for the microstructure observation.

Keywords: Electrophoresis; Ferroelectric properties; SBT; $SrBi_2Ta_2O_9$; Suspensions; Tantalates; Thick films

1. Introduction

$SrBi_2Ta_2O_9$ (SBT) is an important ferroelectric material that has received great attention due to its potential application for non volatile random access memory (NVRAM) as an almost fatigue free material.[1] Although SBT thin films prepared by pulsed laser deposition,[2] metalorganic chemical vapor deposition (MOCVD),[3] and sol-gel process[4] have been largely studied during recent years, these techniques are not appropriate to prepare films with thickness higher than 1–2 μm. To prepare ceramic films with higher thickness, the most used method has been the screen-printing technique,[5,6] which consists in preparing the ceramic pastes and printing them onto the substrates. In spite of the successfulness of the screen printing method, one of its disadvantages is the impossibility of the conformational deposition (homogeneous deposition onto samples with complicated shapes).[7]

In recent years, the electrophoretic deposition (EPD) technique has attracted great interest as a method for the preparation of ceramic thick films[8–10] as a simple, cost effective and low temperature process, besides allowing products of different geometries to be processed. These advantages have made the EPD an economical alternative method to be used commercially,[11] both in ceramic processing and in the preparation of ceramic thick films (thickness higher than 2 μm) on a metallic substrate.

Basically, EPD is a process in which charged powder particles in a suspension are deposited onto an electrode of opposite charge, under the action of an electric field. The choice of the suspending medium is an important parameter in EPD and, normally, organic media (acetone,[12] ethanol,[13] ethanol–acetylacetone,[14] among others) have been preferred. However, few works have focused on the preparation of ceramics by EPD using aqueous suspensions,[15–18] although an aqueous system has the advantages of lower processing cost and lower electric field requirement. Moreover, the search of synthesis and processing methods with a lower environmental

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cost has been intensified recently. The negative aspect in using water as the suspension medium is the electrolysis, which can cause the development of bubbles, corrosion of the electrodes and local heating.

In this study, the main objective is to verify the applicability of EPD using an aqueous suspension to prepare SBT thick films. Different dispersant agents and pH values were investigated to evaluate the EPD characteristics.

2. Experimental procedure

The powder was synthesized by the polymeric precursor method, which is thoroughly described elsewhere.[19] In a brief description, the SBT powder was prepared by the polymeric precursor method which consists in the dissolution of the metallic cations in a citric acid aqueous solution, followed by a polyesterification reaction with ethylene glycol. So, the homogeneous distribution of the cations within the polymeric chain leads to a compound displaying a very good stoichiometry. The crystalline phases of the powder were examined by X-ray diffraction—XRD (Rigaku, DM Max 2500 PC), and the surface area was determined by single point BET adsorption (Micromeritcs, ASAP 2000). The particle size was estimated by BET and by transmission electron microscopy—TEM (Philips, CM 200).

The suspensions were created by dispersing the SBT powder (2.6 g/l; 0.03 vol.%) in deionized water using two different polymers as dispersants: an ester polyphosphate (C213) and an ammonium polyelectrolyte with carboxyl groups (Darvan 821-A, R. T. Vanderbilt, USA) with an ultrasonic horn, for 2 min. The surface properties of the powder were investigated by zeta potential measurements (ZetaPlus, Brookhaven Instrument).

EPD experiments were performed using a power supply (Pharmacia Biotech, EPS 600) operating at constant current. The films were formed on 20×10 mm alumina and 10×10 mm Pt/Ti/SiO_2/Si substrates. The alumina substrates were electroded by screen printing platinum paste followed by sintering at 800 °C for 2 h. The films were prepared using two parallel electrodes placed at a separation distance of 3 mm in the suspension, by a 6 V applied potential and 4 mA current, for 10 min.

The lowest applied voltage allowed for the power source is 6 V (which is high enough to promote the electrolysis of water), so the limitation for this potential was the current. If the current is set on a lower value, it is allowed to diminish the corresponding voltage. At a current of 4 mA, it was possible to achieve a voltage of 4 V. Since the distance between the electrodes was kept at 3 mm, the applied electrical field ranged from 13 to 20 V/cm and the current density ranged from 10 to 13 mA/cm^2. Due to the high diluted suspension, the deposited layer after 10 min was very thin, so several cycles of deposition-drying of the deposit were carried out in order to achieve a thickness of around 5 μm. In this work the films are a six-layers-deposit and each layer was dried under a hot air flux for 1 min before the next one. After the deposition, a thermal treatment ranging from 700 to 1000 °C was performed for times ranging from 0.5 to 2 h.

The microstructure of the films was characterized using XRD and scanning electron microscopy—SEM (Zeiss, DSM 940A). The electrical properties were measured by the hysteresis loops (Radiant Workstation).

3. Results and discussion

3.1. Preparation and characterization of the powders

After an appropriate thermal treatment to eliminate the organic material, the desired $SrBi_2Ta_2O_9$ compound was obtained. The treatment at 700 °C for 2 h is sufficient to achieve a well crystallized single phase material, as showed in Fig. 1.

From the value of specific surface area, measured by BET the particle mean size, D_{BET}, was calculated through the equation:

$$D_{BET} = 6000/S_{BET} \cdot \rho \ (\text{nm}),$$

where S_{BET} is the specific surface area (m^2/g) and ρ is the theoretical density (8.78 g/cm^3). The value of $D_{BET} = 183$ nm is in agreement with TEM results, as can be seen in Fig. 2. The TEM image also shows some agglomerated particles what is normally observed for powders synthesized by wet-chemical methods. These agglomerated particles are easily broken under ultrasonication.

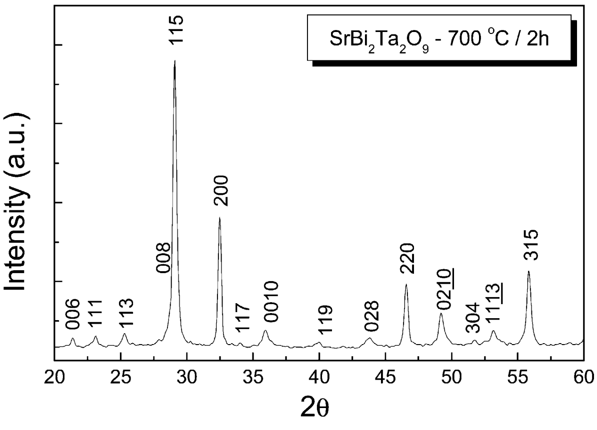

Fig. 1. XRD pattern for the SBT powder treated at 700 °C for 2 h.

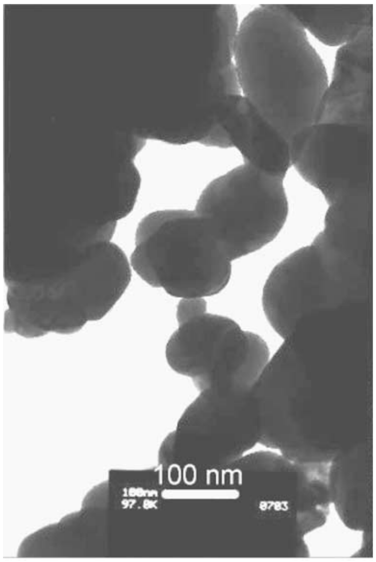

Fig. 2. TEM image of SBT powder treated at 700 °C for 2 h.

3.2. Dispersion of the powder suspension

It was employed a diluted suspension (0.03 vol.%) to minimize particles interactions during their migration by minimization of the flocculation near the electrode, according to Hosseinbabaei and Raissidehkordi.[20] The dispersants were added considering the surface area of the powder at concentrations of 4, 6 and 8 mg/m^2, followed by ultrasonication for 2 min with a 450 W ultrasonic horn.

In water, the powder develops a negative surface potential as measured by the zeta potential measurements. Zeta potential is the potential resulted between the charges adsorbed on the surface of the particles and the free ions in the liquid medium in which these particles are moving.

In order to obtain the thick films, the suspension can be charge stabilized (adding H^+ or OH^- by changing the pH) or sterically stabilized (adding deflocculants). However, if both mechanisms are used, it is possible to reach higher zeta potentials.[15] The increase of the dispersant concentration from 4 to 8 mg/m^2 changed the value of zeta potential from −35 to −27 mV. So, it was used the lower dispersant concentration (4 mg/m^2), which provides the higher absolute value of the zeta potential. Fig. 3 presents the zeta potential versus pH of the SBT powder suspensions with and without dispersants. The iso-electric point (IEP is the pH value for which the zeta potential is zero) of the SBT powder is pH 3.3, i.e. the particle surfaces are positively charged when the suspension pH <3.3, and negatively charged when the suspension pH >3.3. The addition of dispersants changes the IEP towards lower pH values (2.2 and 1.9 for Darvan and C213, respectively).

Although the particles surfaces are negatively charged in a wide pH range when dispersants are added (with zeta potential absolute value approximately 40 mV), the best deposition conditions were obtained when the pH was adjusted to $9<\text{pH}<10$ (zeta values between −50 and −60 mV) by adding NH_4OH. The films deposited using $5<\text{pH}<9$ presented an inhomogeneous microstructure when they had adherence enough to remain on the substrate. In other cases the deposit disintegrated when the substrate was withdrawn from the suspension. For pH >10, a strong gas evolution was observed and the deposit did not adhere to the substrate.

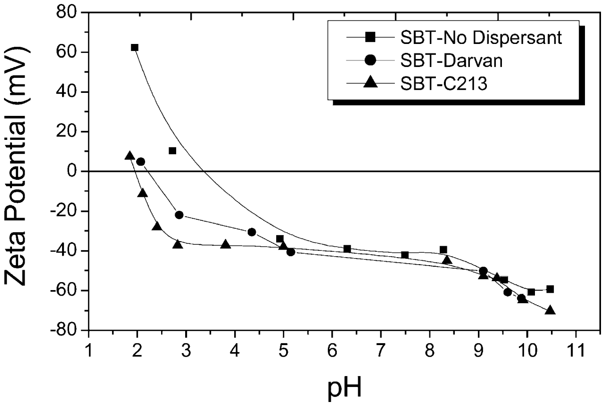

Fig. 3. Zeta potential of the SBT particles with and without dispersants (C213 and Darvan 821-A).

3.3. Deposition and characterization of the SBT films

Fig. 4 displays the crystalline phases of the films deposited onto $Pt/Ti/SiO_2/Si$ substrates, using C213 as dispersant. It can be observed that the films present the same crystalline phases of the original powder, indicating that the EPD process does not change the stoichiometry of the compound at an extension detectable by XRD. This suggests that the obtained SBT powder is chemically stable, presenting no preferential dissolution in the EPD medium, as occurs with PZT in a medium with $\text{pH}<5$. In this case Pb is preferentially dissolved, and the compound loses its stoichiometry, leading to a

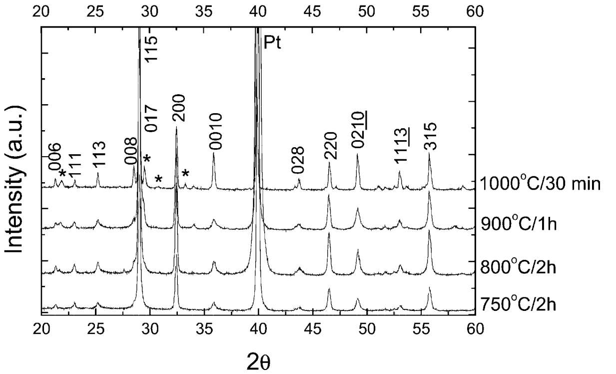

Fig. 4. XRD results for the SBT films deposited by EPD onto $Pt/Ti/SiO_2/Si$ substrates treated at several temperatures, (Dispersant = C213).

film whose crystalline phases are different from PZT.[16] For the film treated at 1000 °C for 30 min, some unknown phases are observed (ascribed by ∗), probably due to interactions between the film and the substrate since this temperature is too high.

The films prepared from suspensions with Darvan did not show any difference in the XRD results. The microstructure of the films prepared using both dispersants and sintered at 750 and 800 °C/2 h is shown in Fig. 5. It can be observed that the films present a surface with some pores, independently of the dispersant used. The advantage of using the C213 dispersant is that the films present bigger grains, what could suggest a better suspension stabilization and a higher deposition rate, since bigger particles could be still dispersed. For this reason, C213 was chosen to prepare the SBT films.

The microstructures, observed by SEM, of the films treated at temperatures from 750 to 1000 °C are displayed in Fig. 6. It can be observed that the films present some pores which may be created by the gas evolution observed during the deposition, what is common when an aqueous suspension is used. To prevent the electrolysis of water, the electric field should be the lowest possible.[18] Even limiting the voltage to 4 V by the low current, in some cases it was observed some gas evolution in the electrode. The gas evolution also affects the density of the deposits leading to a porous microstructure. It can be observed that the pores remain even after sintering at 1000 °C for 30 min. It is noteworthy that the treatment at 1000 °C highly prejudices the substrate and leads to interdiffusion between the film and the substrate and some cracks were also observed (not shown here). Films of thickness >5 μm could be obtained by this process, as can be seen in the micrograph displayed in Fig. 7. The XRD results for the SBT films deposited onto platinum-electroded alumina substrates are shown in Fig. 8. It can be seen that the films present features similar to the ones already observed in Fig. 4.

The films deposited onto alumina (Fig. 9) presented no cracks (observed by optical microscopy, not shown here) and a microstructure with higher surface roughness, due to the roughness of the alumina substrate and also some pores inherent to the EPD process. For the

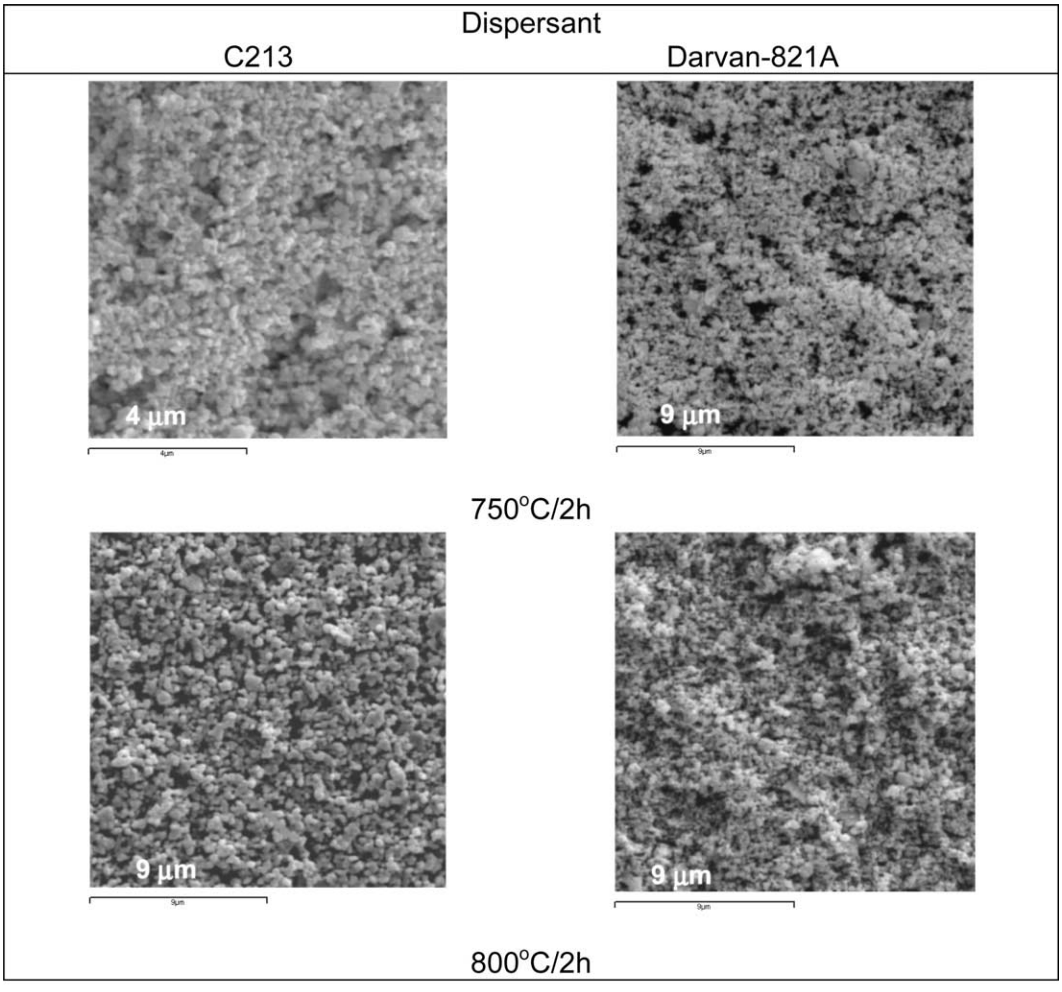

Fig. 5. Microstructure of SBT films using different dispersants deposited onto $Pt/Ti/SiO_2/Si$ substrates, treated at 750 °C/2 h; and 800 °C/2 h.

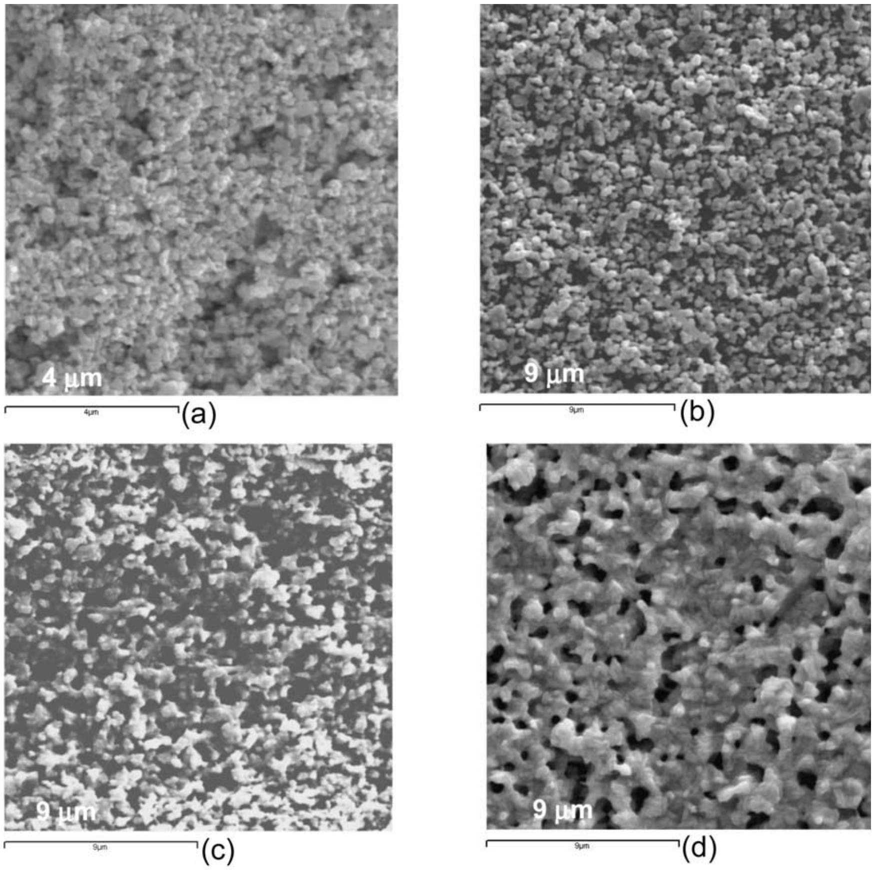

Fig. 6. Sintered SBT films deposited onto Pt/Ti/SiO_2 /Si substrates, treated at: (a) 750 °C/2 h; (b) 800 °C/2 h; (c) 900 °C/1 h and (d) 1000 °C/30 min (Dispersant = C213).

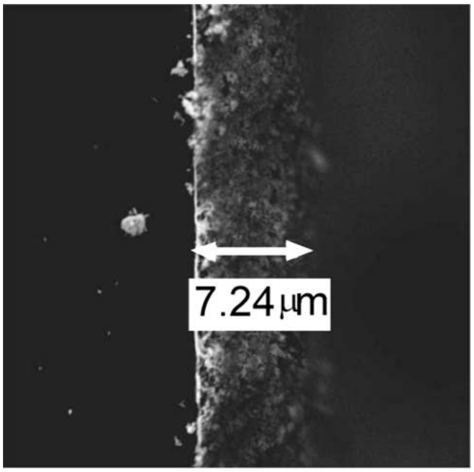

Fig. 7. Micrograph of the cross section of the SBT film deposited onto Pt/Ti/SiO_2 /Si substrate.

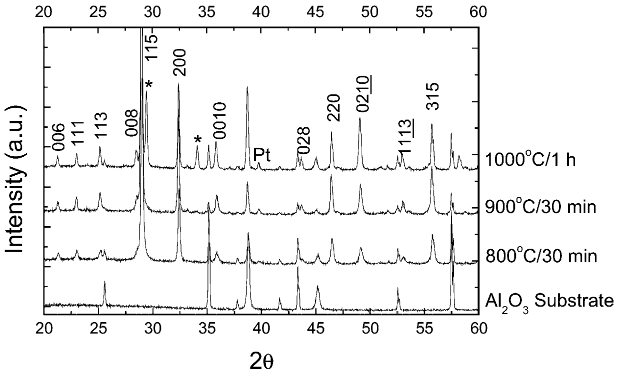

Fig. 8. XRD results for the SBT films deposited by EPD onto Pt-coated alumina substrates treated at several temperatures (Dispersant = C213).

film treated at 1000 °C for 1 h, it is possible to verify the beginning of a sintering process, but the film is still porous.

The electrical measurements were carried out after sputter deposition of Au using a shadow mask, forming the 300 µm diameter top electrodes. The hysteresis loop of the SBT film deposited onto Pt/Ti/SiO_2/Si substrate and heat treated at 800 °C/2 h is displayed in Fig. 10. The ferroelectric characteristics of the film can be observed, with a remnant polarization ($2P_r$) of 4.3 µC/cm^2, under an applied voltage of 250 V. This result is very far from those obtained for SBT thin films or for bulks, probably due to the low density of the thick film.

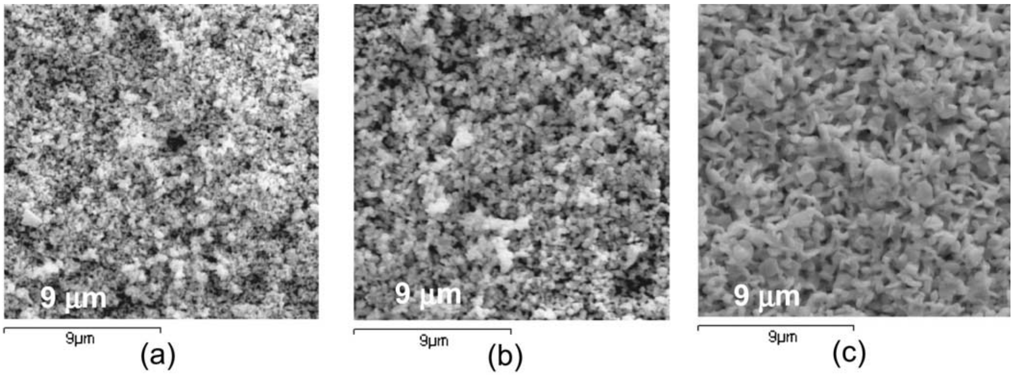

Fig. 9. Sintered SBT films deposited onto Pt-coated alumina substrates, treated at: (a) 800 °C/30 min; (b) 900 °C/30 min and (c) 1000 °C/1h (Dispersant = C213).

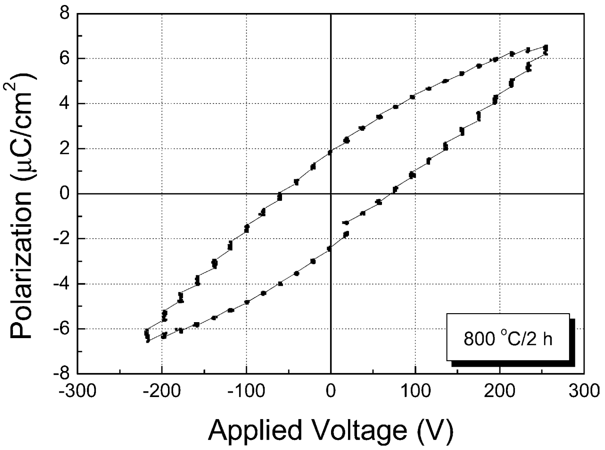

Fig. 10. Electrical measurement for the SBT film deposited onto Pt/Ti/SiO_2/Si substrate treated at 800 °C/2 h.

4. Conclusions

Nanosized SBT powders, prepared by a wet-chemical method, have been used to prepare SBT thick films. An electrophoretic deposition process using water as a suspension medium allowed to obtain films >5 µm thickness. According to the XRD data, the films presented the same crystalline phases of the original powder. No secondary phases, due to partial dissolution of the powder in the EPD medium, were observed, even after sintering, suggesting that the obtained powder is chemically stable. This was confirmed by the electrical properties measured for the film deposited onto Pt/Ti/SiO_2/Si substrate and treated at 800 °C/ 2 h. A remnant polarization ($2P_r$) of 4.3 µC/cm^2 under an applied voltage of 250 V could be achieved. These results are far lower than those obtained for SBT thin films and bulk due to the low density of the deposit, which can be enhanced by changing the suspension properties (suspension powder concentration, conductivity and dispersant). These results indicate the suitability of the EPD process in fabricating ferroelectric SBT thick films, using an environmentally friendly medium. Further studies are in progress to optimize the process conditions in order to improve the quality of the deposits.

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