Materials Research Bulletin 70 (2015) 99–105

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Effect of oxygen-ion motion on dielectric properties of $Ba_{0.6}Sr_{0.4}TiO_3$ thick films

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ARTICLE INFO

Article history:
Received 3 September 2014
Received in revised form 10 March 2015
Accepted 12 April 2015
Available online 14 April 2015

Keywords:
A. Oxides
C. Impedance spectroscopy
D. Defects
D. Dielectric properties

ABSTRACT

The dielectric properties and electrical conductivity of porous $Ba_{0.6}Sr_{0.4}TiO_3$ thick films prepared by screen printing were investigated. The thick films displayed several anomalous dielectric behaviors differing from dense $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics. The AC conductivity data obeyed the power-law relation of the universal dielectric response model, suggesting the existence of polarization resulting from hopping carriers in the thick films. Impedance spectroscopy analysis indicated two separate contributions for the thick films, both corresponding to the response of the grains. The activation energies of the two response processes were determined to be ~1.0 eV, manifesting that oxygen ions were the mobile carriers. The electrical heterogeneity of the grains was interpreted in relation to the porosity of the thick films. The dielectric anomalies of the thick films were linked to oxygen-ion motion. This work highlights an important effect of oxygen-ion hopping on the dielectric loss of the thick films in a wide frequency range.

1. Introduction

In the past decades, the dielectric nonlinearity of barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$, BST) under bias electric field has been the subject of extensive investigations. This desired property makes BST a promising candidate material for electrically tunable microwave devices, such as filters, resonators, delay lines, variable capacitors and phase shifters [1,2].

Realization of BST thick films in the tunable microwave devices has attracted continuous attention [3–9]. BST thick films integrate the merits of their thin film and ceramic counterparts, allowing convenient preparation process, low bias voltages for tuning and good nonlinear dielectric properties. Moreover, the thick-film tunable devices accommodate the demands of miniaturization, complexity and multilayer assembly. Among various techniques for preparing BST thick films, screen printing is cost-effective and flexible in producing complicated and diversified patterns [3]. In view of the tunable device applications, the dielectric properties of screen-printed BST thick films in various frequency ranges have been investigated [4–6]. Moreover, the performance of prototype microwave devices based on screen-printed BST thick films has been evaluated [7–9].

Screen-printed BST thick films are susceptible to deleterious reactions with the substrates occurred during sintering. To avoid the undesired reactions, the thick films were usually sintered at temperatures less than 1250 °C, resulting in porous microstructures [8]. These porous thick films displayed anomalous dielectric behaviors, discrepant from their dense ceramic counterparts [4–6]. Essentially, the dielectric properties of a material are determined by the response of involved polarization mechanisms. In this sense, the dielectric anomalies of the thick films should be closely relevant to extrinsic polarization species stemming from the porous microstructures. Attempts have been made to explain the dielectric anomalies of the thick films [4,5,10]. Nonetheless, more efforts are needed to better understand the underlying mechanisms, especially the origin of the extrinsic polarization species in the porous thick films and their contributions to the dielectric properties.

In this work, we study the dielectric behaviors and electrical conductivity of screen-printed $Ba_{0.6}Sr_{0.4}TiO_3$ thick films. The purpose is to enhance the understanding of the extrinsic mechanisms contributing to the dielectric properties of the thick films.

2. Experimental

All the raw materials used in this work were commercially available reagent grade chemicals (Sinopharm Chemical Reagent Co., Ltd.). $Ba_{0.6}Sr_{0.4}TiO_3$ powders were synthesized by a citrate method [11]. The powders were calcined at 600 and 850 °C, respectively. The calcined powders had a single perovskite phase and their average particle sizes were 60 and 120 nm, respectively.

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http://dx.doi.org/10.1016/j.materresbull.2015.04.023
0025-5408/

The thick films were prepared by screen printing (S-200HF flat surface screen printer, Pad Printer Engineering Co., Ltd.). The two calcined powders were mixed at a weight ratio of 1:3 to prepare starting powder. The ink for screen printing was prepared from the starting powder and an organic medium at a solid loading of 65 wt. %. The organic medium was composed of ethyl cellulose (5 wt.%), terpineol (91 wt.%), 2-(2-butoxyethoxy)ethyl acetate (2 wt.%), polyethylene glycol (1 wt.%) and dibutyl phthalate (1 wt.%). Platinum paste was screen printed onto aluminum substrates as bottom electrode and sintered at 1300 °C for 2 h. Then the ink was printed on the bottom electrode and heated at 600 °C for 1 h. This procedure was repeated for three times. Afterwards, the thick films were sintered in air for 2 h at 1200 and 1230 °C, respectively. Finally, sliver paste was printed on the thick films as top electrode and sintered at 800 °C for 0.5 h in air. The areas of the top electrodes for the thick films sintered at 1200 and 1230 °C were 6.6 and 7.1 mm^2, respectively. This preparation process was basically identical to our earlier report [10], except for a composition modification of the ink in the present work.

For comparison purposes, $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics were prepared from the powder calcined at 600 °C. The powder was uniaxially pressed into discs of 13 mm in diameter and 1 mm in thickness. The compacted discs were sintered at 1260 °C for 2 h in air. The ceramic specimens attained ~95% of the theoretical density.

The microstructure of the thick films was observed at a Jeol JSM-5610LV scanning electron microscope (SEM). The characteristic parameters of the microstructures were determined using the Image Profession Plus software. The porosity of the thick films was estimated by counting black and gray pixels of the images, which refer to pores and grains, respectively [12].

The dielectric constant (ε_r) and the loss ($\tan\delta$) were measured between −70 and 120 °C using a TH2828 precision LCR meter (20 Hz–1 MHz) and a SSC-M10 environmental chamber (C4 controller). The AC conductivity was measured between room temperature (20 °C) and 120 °C using the same set-up. The DC resistivity was measured under 50 V/cm at room temperature using a Radiant precision workstation. The nonlinear dielectric properties under bias electric field were measured at room temperature using a TH2818 automatic component analyzer at 10 kHz. A blocking circuit was adopted to protect the analyzer from applied bias voltages. The complex impedance spectrum was measured between 340 and 420 °C using the TH2828 LCR meter and a program-controlled oven (home-made). The measured data were analyzed using the Zview 3.1a software.

3. Results and discussion

3.1. Structure and nonlinear dielectric properties

X-ray diffraction (XRD) analysis identified a cubic perovskite structure for the ceramic and thick film specimens (not shown here). Fig. 1 shows the typical morphology of the thick films, illustrating a porous microstructure. The microstructural parameters of the thick films are listed in Table 1. The thick film sintered at 1230 °C achieved a lower porosity (~17%) than that sintered at 1200 °C. This porosity value is decreased compared with our previous result (~20%) for the thick film sintered at 1250 °C [10], which can be attributed to the composition modification of the ink employed in the present work.

The nonlinear dielectric properties of the thick films are listed in Table 2. For comparison purposes, the data of the ceramic specimen are also included in the table. The dielectric constant and the loss were measured at zero bias field. The tunabilities of the ceramic and thick film specimens were calculated as the percentages of dielectric constant change at 20 and 66 kV/cm, respectively. The figure of merit (FOM), the criterion to evaluate the overall nonlinear dielectric properties, was determined from the ratio of the tunability and the dielectric loss [13]. The thick film sintered at 1230 °C showed better nonlinear dielectric properties, which can be readily explained with respect to its lower porosity (Table 1). Moreover, its dielectric loss (1.0%) is reduced compared with our previous result (1.4%) for the thick film sintered at 1250 °C [10].

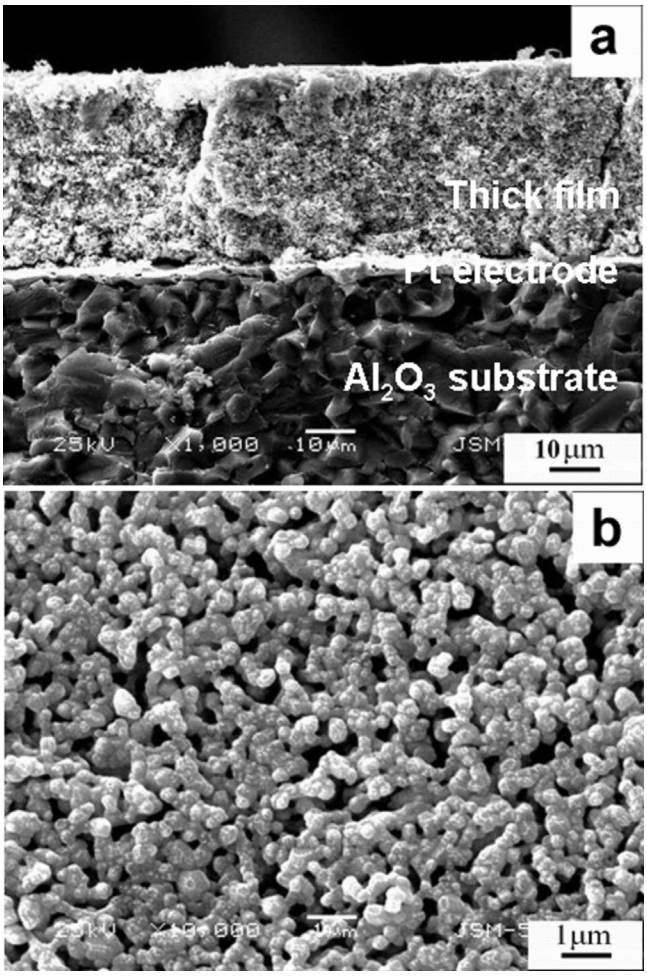

Fig. 1. SEM images of the thick film sintered at 1230 °C: (a) cross-sectional and (b) surface views.

As shown in Table 2, the dielectric losses of the thick films were evidently larger than the ceramic specimen, unfavorable for achieving a high FOM. This phenomenon is ascribed to the porous nature of the thick films. DC resistivity measurement indicated that the resistivity of the ceramic specimen was $1.6 \times 10^{12}\,\Omega$ cm, while the results of the thick films sintered at 1200 and 1230 °C were 1.4×10^{12} and $1.2 \times 10^{12}\,\Omega$ cm, respectively. These data, quite close in magnitude, suggest that leakage dissipation is unlikely to be the dominant reason for the evidently larger dielectric losses of

Table 1
Microstructural parameters of the thick films sintered at different temperatures.

Sintering temperature (°C)	Porosity (%)	Average grain size (nm)	Thickness (μm)
1200	23(±1)	250(±10)	40(±2)
1230	17(±1)	270(±10)	38(±2)