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Conductive atomic force microscopy characterization of PTCR-$BaTiO_3$ laser-sintered ceramics

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ABSTRACT

Thermistor ceramics based on $BaTiO_3$ (BT) with a positive temperature coefficient of resistivity (PTCR) are widely used for sensor applications in the semiconductor industry. The distinct properties of the ceramics depend on the conditions used to process them. In this work, a laser sintering technique was employed to produce $BaTiO_3$:La,Mn ceramics for the first time. In this technique, a CO_2 laser was used as the main heating source and no atmosphere control was employed. The ceramics sintered at a power density of 5.5 W/mm^2 for 1 s presented high relative density, homogeneous microstructures, and a PTCR jump of three orders of magnitude. From simultaneous electrical and topographical images obtained via conductive atomic force microscopy (C-AFM), it was possible to estimate the depletion layer in PTCR-BT ceramics to be at about 600 nm. The results presented here support the core–shell model employed to explain the electrical microstructure in PTCR-BT ceramics.

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1. Introduction

Perovskite-structured $BaTiO_3$ (BT) has a relatively high tolerance for many cation dopants, which are normally used to engineer the electrical properties of the material. In this way, BT has found a number of electro-optic, electromechanical, and dielectric applications [1–3]. Nevertheless, as recognized in literature, the largest commercial markets for this material seem to still be positive temperature coefficient of resistivity (PTCR) and multilayer ceramics capacitors (MLC) [1,4,5]. For these applications, the formulation often involves the incorporation of rare-earth (RE) cations into the host material [6–9], the resulting electrical properties is strongly affected by the change in the occupational sites in the perovskite lattice. Donors such as rare earths often occupy the Ba^{2+} site in the grain regions, whereas acceptors such as Fe^{3+} and Mn^{2+} for the Ti^{4+} ions are segregated at the grain boundaries [4,6]. Donors are used to induce semiconductivity in the grains whereas acceptors act as electron traps at the grain boundary regions. This chemical heterogeneity gives rise to an *n*–*i*–*n* type structure between adjacent grains due to the creation of Schottky barriers at the grain boundaries [5,6,10].

The currently accepted model to explain the PTCR effect was firstly proposed by Heywang in 1961 and modified by Jonker in 1964 (Heywang–Jonker model) [6,11]. According to Heywang, the increase of the electrical resistivity of the material is attributed to the arising of a potential barrier in the grain boundaries region because of the presence of acceptor states in this region forming a bidimensional layer of electron traps [4–6]. The height of the potential barrier is inversely proportional to the dielectric permittivity. Starting from Curie temperature, the permittivity reduction leads to a positive coefficient of resistivity as a function of the temperature due to the conductivity depends of the potential barrier height [4–6]. Jonker proposed a complementary model based on ferroelectric behavior of the tetragonal BT to explain the low resistivity below Curie temperature [6]. In this model, the spontaneous polarization could cancel out the potential barrier in regions along the polarization perpendicular to the grain boundary because of the creation of surface charges in this region. Later, in 1976, Daniels and Wernicke [12,13] introduced a defect chemical model that characterizes the nature and behavior of the electrically charged point defects that are responsible for the development of the PTCR effect in $BaTiO_3$, which is not clarified by Heywang's or Jonker's models. According to the authors, two conditions must be satisfied to make BT semiconducting ceramics: (i) oxygen deficiency by intrinsic reduction and (ii) donor doping. PTCR properties only appear, however, in the case of donor doping. The model proposed

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by Daniels and Wernicke is related to the metal vacancy formation when donor dopants are added. More recently, Fiorenza et al. in 2009 [10], by means of the conductive atomic force microscopy (C-AFM) technique, proposed a core–shell model to explain the PTCR response in BT ceramics. The authors suggest that the grain system's structure has three distinct regions. The outer layer is an oxidized, insulating grain boundary region; the intermediate layer is a deoxidized, semiconducting outer-grain region, and the inner layer is an oxygen-deficient grain interior, which is again a semiconducting inner-grain region.

It is well known that there is a strong relationship between the electrical properties of the ceramic materials and their processing conditions. Recently, the laser sintering technique has been presented as an alternative unconventional technique [3,14] wherein a CO_2 laser is used as the main heating source. The main advantages of this method are the following: rapid processing; the potential for using high heating and cooling rates (about 2000 °C/min) without crucibles, thereby reducing the risk of contamination; and the potential for sintering materials with high melting points.

Additionally, the C-AFM is unique to probe electrical characteristics with nanometer-scale resolution [15–17], and over the last few years it has been widely used for investigating local electrical properties on semiconductors, film dislocation, carrier profiling and charge injection [18–21]. Moreover, in combination with complementary atomic force microscopy (AFM) modes, C-AFM enables correlating nanoscale structure and electrical function at the same sample location. As indicated by its name, C-AFM is intimately related to AFM [22]. In C-AFM an electrically conducting AFM tip is used as a movable electrode in a conventional AFM setup. The tip is brought into contact with the surface at the position of interest, with a user-specified applied force which is maintained by the AFM's feedback electronics. In the current C-AFM image mode, a constant voltage is applied between the tip and the counter electrode and the current is recorded while the tip is scanned over the sample surface. This provides a spatial map of the local sample conductivity. The sample topography can also be measured simultaneously, making it possible to correlate spatial variations of the conductivity with the topography.

Therefore, in this study we had as objective the production of PTCR-$BaTiO_3$:La,Mn ceramics using an alternative sintering technique, laser sintering. The sintering was performed in open atmosphere and the electrical characterization of the samples was done by the impedance spectroscopy and C-AFM techniques.

2. Experimental procedure

$Ba_{0.998}La_{0.002}Ti_{0.999}Mn_{0.001}O_{3+\delta}$ powders were synthesized by the solid state reaction method using $BaCO_3$ (Synth 99%), TiO_2 (Aldrich, 99.9%) La_2O_3 and (Aldrich, 99.9%) and MnO (Synth 99%) as precursor materials. δ symbolizes the off-stoichiometry on the oxygen site. The precursors ($BaCO_3$, TiO_2 and La_2O_3) were ball milled with zircon balls for 48 h and calcined at 1250 °C/5 h. After calcination, the powder was ball milled again for 6 h in order to decrease the powder agglomeration. In order to favor the emergence of acceptor states in the grain boundary region due to high heating and cooling rates during the laser sintering, the manganese addition was made by mixing the MnO to the $BaTiO_3$:La powder, ball-milling for 12 h and dividing the resultant material into two parts. The first portion was laser-sintered without intermediate calcination (named BT-N) and the second was calcined at 1250 °C for 2 h, ball milled for 6 h and then laser-sintered (named BT-C).

Next, the calcined powder was mixed with a binder solution of polyvinyl alcohol (PVA) in a concentration of 0.1 g/ml, and uniaxially compacted at about 120 MPa (green density of (55 ± 3)%) into disk-shaped samples with 4 mm in diameter and 1.5 mm thick. The sintering was then performed using a CO_2 laser (GEM-100L—Coherent) in continuous mode as the main heating source: the laser sintering technique. In this technique, the samples were placed on a base composed of the same material to be sintered, and the laser beam (diameter: 4.6 ± 0.3 mm) was directed and held at the center of the sample throughout the sintering process. The base composition and the laser beam diameter play an essential role in the reduction of the heat exchange between the ceramic and environment, thus minimizing temperature gradients. After a pre-heating stage at 200 °C, the laser power was raised at a linear rate of 0.01 W/mm^2s up to 0.28 W/mm^2 and held at this value for 15 s. This initial power-ramping stage was used to decrease the thermal gradient in the sample, inhibiting the formation of cracks. Afterwards, the power density was raised again, at a linear rate of 0.03 W/mm^2s, up to (5.5 ± 0.1) W/mm^2 for 1 s. After the irradiation of the first sample face, the process was repeated on the opposite face. Using these procedures the total PTCR-BT laser sintering time was 8 min, which is significantly faster than the conventional sintering in an electric furnace, which takes several hours. The temperature during laser sintering was measured using a type S thermocouple (cross-section = 0.25 mm) positioned at the center of the sample surface [23]. Note that the whole process of synthesis and sintering was conducted in air.

Density of the ceramics was determined by using the Archimedes principle. X-ray diffraction (XRD) measurements were performed in a Rigaku diffractometer RINT 2000/PC using Cu Kα radiation with 2θ range between 20° to 60° in continuous-scan mode using steps of 0.02°. The morphological characteristics of the samples were analyzed through scanning electron microscopy (SEM) (Jeol, JSM 6510LV) and the average grain size (AGS) was evaluated according to the well-known Intercept Length method. For electrical characterization, electrical contacts were formed on both major surfaces of the polished ceramics by applying Pt paste, followed by firing at 700 °C for 30 min. The measurements were carried out using a Solartron 1260 Impedance Analyzer controlled by a personal computer, during a period of cooling from 325 to 25 °C, in the frequency range of 1–10 MHz with an applied potential of 500 mV. The impedance spectroscopy results were processed in terms of complex impedance [$Z^* = Z' - j\,Z''$] and were converted into real resistivity data after taking into consideration each sample geometry factor and the brick layer model [24].

All C-AFM measurements were performed at room temperature and atmospheric pressure using a commercial AFM (Multiview4000^{TM}, Nanonics) system equipped with a current-sensing C-AFM module. In the C-AFM measurements, conductive Pt tips with diameters between 100 and 300 nm scanned over the sample surfaces in the tapping mode under DC Bias. Positive-bias voltages were applied to the bottom electrode of silver paint on the face opposite to the scanned BT-N ceramic surface while the tip was grounded. The current between the tip and sample was measured simultaneously with the surface topography imaging, allowing direct correlation of structural features with their electrical characteristics. In this study, the images were obtained in two ways: (i) the ceramics were only polished and no further treatment was performed (BT-NP), and (ii) the ceramics were polished and chemically etched prior to the C-AFM measurements (BT-NE).

3. Results and discussion

An important parameter to be defined in laser sintering is the power density (power/area) incident on the sample surface, which is directly related to the temperature achieved for the sample. In an analogy to the conventional sintering process in an electric furnace, a point-to-point dilatometric curve for the laser-sintered ceramic was obtained. Fig. 1 shows the results of axial (parallel to the

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