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The influence of post-sintering re-oxidation treatment on dielectric response of dense and porous $Ba_{0.70}Sr_{0.30}TiO_3$ ceramics

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Abstract

The effects of post-sintering re-oxidation treatment on dielectric relaxation, conductive and non-linear properties of dense $Ba_{0.70}Sr_{0.30}TiO_3$ ceramics and its porous homologs were discussed. The ceramics were prepared by solid state reaction and sintered at 1450 °C/2 h. The porosity degree was induced by adding 35 vol% graphite as sacrificial pore forming agent into $Ba_{0.70}Sr_{0.30}TiO_3$ powder. A comparative impedance spectroscopy study was performed for the (i) as-sintered and (ii) after a post-sintering re-oxidation thermal treatment of both types of ceramics. The impedance spectroscopy analysis revealed that as-sintered dense and porous $Ba_{0.70}Sr_{0.30}TiO_3$ ceramics exhibit a giant relaxation with a shift of the transition temperature from ~34 °C to above ~117 °C, in the frequency range of (20 kHz, 1.5 MHz), and a decrease of dielectric permittivity with increasing porosity. The presumption of presence of oxygen vacancies in the grain boundary of as-sintered $Ba_{0.70}Sr_{0.30}TiO_3$ ceramics is validated by electrical inhomogeneity as revealed by the existence of two components in the complex impedance spectra. After a post-annealing treatment at 1100 °C for 36 h, the dielectric response is completely changed: the permittivity *vs.* temperature dependences present maxima located at around $T_m \approx 35$ °C, with almost no frequency dispersion, the dielectric losses are dramatically reduced and the complex impedance spectra present a single arch component, confirming the electrical homogeneity for both dense and porous samples. For both the investigated samples it was found that zero field permittivity $\varepsilon(0)$, and the values of the relative tunability are also affected by the re-oxidation treatment.

Keywords: A. Sintering; C. Ferroelectric properties; C. Dielectric properties; Porous ceramics; Oxygen vacancies

1. Introduction

$BaTiO_3$-based ceramics are the main constituents of various electronic components in microelectronics, such as multilayer ceramic capacitors, positive temperature coefficient of resistivity thermistors, electro-optic devices, piezoelectric transducers and tunable elements. Its solid solutions were extensively employed to tailor ferroelectric–paraelectric phase transitions and their functional properties required by specific applications towards desired values. The system $BaTiO_3$–$SrTiO_3$ ($Ba_{1-x}Sr_xTiO_3$) represents one of the well-known $BaTiO_3$-based solid solutions, with full solubility across all the compositional range (x) [1–4]. $Ba_{1-x}Sr_xTiO_3$ (BST) solid solutions have been intensively investigated in the last years mainly for their non-linear dielectric character (*i.e.* field-dependent permittivity $\varepsilon(E)$ or tunability) which are highly attractive for wireless communication industry [5–8]. The increase of strontium amount (x) is usually employed to reduce the Curie temperature in order to tailor the permittivity and dielectric loss level, and to maintain a relatively weak temperature dependence of the dielectric

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constant. BST is extensively used in electrical devices such as microwave phase shifters, tunable oscillators, varactors and multilayer ceramic capacitors.

The properties of solid state materials are determined by their composition, microstructures, but also by micro/nanostructural and charged point defects. Charged defects play an important role on the electrical properties of materials. In particular, the level, distribution and diffusion kinetics of oxygen vacancies, which are the most important and relevant defects in many oxides, are recognized to substantially change their dielectric and conductive properties. In perovskite oxides, oxygen vacancies are preferentially formed in acceptor doped ceramics or in nominally undoped materials with charged impurities as result of the charge compensation. Oxygen vacancies may also be generated under local reducing conditions or as result of fast cooling conditions from the sintering temperature down to the ambient temperature [9–13]. The reported dielectric properties of $BaTiO_3$ and $SrTiO_3$-based materials are often affected by dielectric relaxations originated from accidentally formed oxygen vacancies. However, such effects were not always described in terms of extrinsic contributions. Low-frequency dielectric relaxation phenomena with maximum permittivity *vs.* temperature not associated to the ferroelectric–paraelectric phase transition and a strong frequency shift with increasing temperature were found in perovskites as $BaTiO_3$, $CaTiO_3$, $PbTiO_3$, $SrTiO_3$-based systems [10,11,13–18]. Such low-frequency dielectric relaxations, particularly active at high temperatures of about (400–700) K, were explained as related to oxygen-vacancies generating electrical conduction phenomena in perovskites [18]. High temperature relaxations in the range of (200–400) °C were also found in $(Ba,Sr)TiO_3$ ceramics [11]. The large majority of these papers reported such relaxation phenomena in the paraelectric state, at temperatures much higher than the corresponding Curie temperatures of the ferroelectric perovskites. When such relaxations are overlapped onto the ferroelectric–paraelectric phase transition, they change its shape from a sharp $\varepsilon(T)$ dependence into a diffuse one, with a shift of the maximum permittivity towards high temperatures when the frequency increases, as reported for $Ba(Zr,Ti)O_3$ solid solutions [13]. Such permittivity relaxations have a completely different origin (extrinsic contributions) than the ferroelectric relaxor character of Pb-based solid solutions [19,20].

In the present paper, the role of sintering/post sintering thermal treatments on the dielectric, conductive and non-linear properties of dense $Ba_{0.70}Sr_{0.30}TiO_3$ (BST) ceramics and its porous homolog are reported. A comparative impedance spectroscopy study was performed for as-sintered BST ceramics by comparison with ones obtained in samples after a re-oxidation post-sintering thermal treatment. The aim was to check if the porosity level plays any role on the oxygen vacancies – related dielectric relaxation effects.

2. Experimental details

Dense and porous BST ceramics were prepared by a solid state method from stoichiometric high purity $BaCO_3$ (Merck purity $>99\%$), $SrCO_3$ (Aldrich purity $>99.9\%$), and TiO_2 (Degussa P25 purity $>99.5\%$) oxide powders, calcined and then sintered at 1450 °C/2 h. A detailed presentation of ceramic preparation procedure is reported in a previous paper [21]. In order to avoid the formation of cleavage in the graphite–BST powder mixtures during pressing, the green mix pellets were die-pressed only at 50 MPa, while the pure BST powders were die-pressed at 100 MPa in 30 mm diameter dies and then cold-isostatically pressed at 300 MPa. The ceramic samples analyzed in this study are denoted in the following as *BST0* (dense BST ceramic) and *BST35* for porous BST ceramic, according to the amount of graphite added as pore forming in the BST powder. In order to perform the electric measurement on BST ceramics, silver paste electrodes were deposited on the plane-parallel surfaces of the ceramic pellets. Impedance spectroscopy measurements were carried out in the frequency range of $(20–2\times10^6)$ Hz at temperatures between 25 and 200 °C using an Agilent E4980A Precision RLC type bridge. The non-linear dielectric properties were measured at room temperature on Ag-electroded ceramic disks immersed in transformer oil, under high voltages produced by a function generator coupled with a TREK 30/20A-H-CE amplifier [22]. Room temperature $P(E)$ loops were recorded under a sinusoidal waveform of amplitudes $E_0=(0–8)$ kV/mm for frequency of 10 Hz with a modified Sawyer-Tower circuit. In order to find the differences induced by various oxygen deficiency levels, a re-oxidation post-sintering thermal treatment at 1100 °C for 36 h in air was performed, followed by a slow cooling down to the room temperature. The properties of re-oxidized BST ceramics have been compared with the as-sintered ones.

3. Results and discussions

The relative density of the sintered BST ceramics as determined by Archimedes method shows a maximum of 97% for *BST0* ceramics, while after addition of 35% graphite as pore former, it reduced down to 71% for *BST35*. The structural analysis showed the formation of the pure perovskite phase for both dense and porous ceramics, and homogeneous microstructures, as shown in Fig. 1 [21], which remain unchanged after the post-annealing treatment at 1100 °C/36 h.

3.1. Complex impedance diagram

The complex impedance plots obtained at room temperature for the two types of BST ceramics (as sintered and after thermal treatment at 1100 °C/36 h in air followed by slow cooling) are comparatively shown in Fig. 2. Both as-sintered dense and porous ceramics present two well-defined impedance components: one small semicircle at high frequency (small values of the corresponding impedances) and a large fragment of semicircle towards lower frequencies, corresponding to high impedances (Fig. 2a). These two semicircles suggest the existence of various regions within the ceramic samples characterized by different electrical properties in terms of permittivity and conductivity, which can be described by