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Dielectric investigations in nanostructured tetragonal $BaTiO_3$ ceramics

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ABSTRACT

In this paper, structural and dielectric properties of $BaTiO_3$ ceramics obtained under extreme conditions were investigated. The temperature dependent dielectric investigations revealed that the phase transition temperatures of the $BaTiO_3$ ceramics were raised as a function of residual strains associated to the nanostructuration, while structural characterizations showed a tetragonal arrangement at room temperature. From the frequency dependence analyses of the imaginary parts of dielectric permittivity, impedance and modulus function, three relaxation processes were identified. Two of them exhibit activation energies of 0.45 and 0.63 eV, and were attributed to single and double-ionization of oxygen vacancies. The whole set of results also indicated that the electrons resulting from the ionization of oxygen vacancies are trapped and do not contribute to the electrical conductivity, while the physical properties of the analyzed samples were enhanced by retaining a strained microstructure.

1. Introduction

Barium titanate, $BaTiO_3$ (BTO), is one of the most used ferroelectric material in the electronic industry, finding extensive applications as dielectric material in multilayer ceramic capacitors (MLCCs), piezoelectric actuators, electro-luminescent panels, pyroelectric detectors, embedded capacitance in printed circuit boards, positive temperature coefficient of resistivity (PTCR) sensors, controllers, and pulse generating devices [1]. It belongs to the perovskite-type ferroelectrics, such as PZT ($Pb(Zr,Ti)O_3$) and PMN ($PbMg_{1/3}Nb_{2/3}O_3$), although the unit cell symmetry is temperature dependent. A ferroelectric to paraelectric phase transition occurs at $T_C \sim 400$ K (Curie temperature), above which BTO is cubic. Below the Curie temperature, the structure is slightly distorted, assuming a tetragonal symmetry [2,3]. In this phase, ferroelectricity arises due to the relative displacement of positive and negative charges from the centrosymmetric position of the perovskite unit cell. In fact, in BTO single-crystals and well-crystallized large-grain polycrystals the tetragonal phase is stable between ~280 K and 400 K, and below 280 K the structure becomes orthorhombic, while a further transition for a rhombohedral phase occurs at ~190 K [2,3].

The dielectric properties of bulk ferroelectrics result from the combination of intrinsic (i.e., the response related to orientation of dipoles expected from a single domain crystal with well-defined boundary conditions) and extrinsic (like those associated with domains structure, grain boundaries, and defects) effects [3,4]. Both contributions are generally influenced by grain size distribution [3]. As ferroelectrics find increasing possibilities in micro and nanoelectronic devices, the effects of grain size distribution on their physical properties have been subject of intensive investigation in the last years [5–9]. Nowadays, it is well accepted that as the grain sizes are reduced to the sub-micron level, the dielectric permittivity at room temperature increases, and the temperature dependence of the dielectric permittivity is modified significantly below the Curie temperature [5]. Several researchers observed that polycrystalline BTO exhibits an enhanced dielectric response for samples prepared with a grain size distribution as small as 1 μm. Arlt et al. [10] showed that this behavior is related to the reduction of ferroelectric domains width with grain size reduction, resulting in enhanced mobility of the 90° domain walls. For smaller grain sizes, however, a strong decrease of the relative dielectric constant was reported [5]. The decreasing of the permittivity observed at grain sizes below 1 μm correlates to structural changes. In fact, it is observed that the crystal structure at room temperature becomes progressively less tetragonal and the heat related to the tetragonal to cubic transition is reduced with reducing grain size [3,10,11]. In other words, a change from tetragonal to pseudocubic structure gradually takes place by reducing grain sizes distribution. Thus, for submicron polycrystalline BTO there is a coexistence of different ferroelectric phases at room temperature. Uchino et al.

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[11] showed that the Curie point of BTO shifts to lower temperatures as grain size decreases. A critical particle size around 0.12 μm was determined, for which the Curie point drops bellow room temperature. Besides the shift in Curie temperature, the behavior of the ferroelectric–paraelectric phase transition is also affected by grain size. The typical peak present in permittivity versus temperature curves at the Curie point becomes broader, and its maximum value is reduced with decreasing grain size, becoming almost undistinguishable for particles under 50 nm [3,10]. Frey et al. [12] interpreted these results in terms of a brick-wall model for the distribution of different dielectric phases in a diphasic dielectric. This model considers that the sample is composed by two distinct dielectric phases connected in series: the primary or interior phase's grains, which are isolated by a secondary continuously connected boundary phase. Considering macroscopically single-phased BTO ceramics, Frey et al. [12] proposed that the interior of the grains would undergo the normal ferroelectric transformation, while the series connected low-ε' grain-boundary region dilutes the overall relative dielectric constant at all temperatures. As the grain size decreases, the boundary area per grain volume ratio increases and the dilution effect becomes more pronounced [12]. Furthermore, orthorhombic to tetragonal and rhombohedral to orthorhombic transition temperatures are also affected by grain size distribution, both shifting towards higher temperatures [4,8]. Arlt et al. [10] argue that this is a result of the existence of tensile stresses in the grains acting against the structural changes.

The size dependence of polarization, Curie temperature and tetragonal distortion (c/a, where c and a are unit cell parameters) of the ferroelectric phase has been calculated by means of theoretical models based on the Landau–Ginsburg–Devonshire theory in the case of isolated particles [14–19]. However, there are many causes for size effects in ferroelectrics and is often difficult to separate true size effects from other factors that change with particle/grain size [16–19]. The stability of the ferroelectric phase can be determined by additional factors like defect chemistry, incorporation of foreign atoms and bulk hydroxyl groups, aggregation level of particles, porosity level, residual stresses, etc. [3,20,21]. In fact, it has been theoretically demonstrated that besides grain size, internal stresses also affect the structural, ferroelectric and dielectric properties of fine grained BTO ceramics [22,23]. An additional consideration concerns the electrical boundary conditions in ferroelectric materials. The spontaneous polarization creates depolarization fields that require compensating charges near or at the surfaces/interfaces [19–28]. If for some reason a spontaneous polarization would not be compensated by charge, the consequence of the necessary boundary condition of zero polarization at the free surface would be an internal electrical field oriented in opposition to the polarization itself. In the absence of compensating charge, the depolarization field can, in principle, become strong enough to exceed the free energy reduction for the ferroelectric transition for a given volume of material. Thus, the ferroelectric phase can become thermodynamically unstable. However, this phenomenon is never seen in bulk ferroelectrics because of the numerous mechanisms for its compensation.

In this paper, the dielectric behavior of BTO nanostructured ceramics, obtained under extreme conditions, is presented and discussed. The results show that structural transitions were mainly affected by strain into grains and that these strains also contribute to enhance the physical properties of the studied samples. The presence of oxygen vacancies also contributes to the dielectric properties of the material, producing two relaxation processes that are attributed to single and double-ionized vacancies with activation energies of 0.45 and 0.63 eV, respectively.

2. Experimental procedure

BTO nanostructured ceramics were processed by applying multiple step high-energy ball milling (HEBM), spark plasma sintering (SPS) and oxidative post-sintering heat treatments as previously reported [24]. Phase identification was performed by using a Shimadzu XRD-7000 X-ray diffractometer with Cu K_α radiation. Crystallographic parameters were refined through Rietveld analysis using the FullProf software [25]. Surface scanning electron microscopy (SEM) images were obtained in the secondary electron detector mode by using a Shimadzu SuperScan SS-550 microscope. Gold electrodes were sputtered in both ceramic surfaces prior dielectric characterizations. Computer assisted dielectric investigations, by using an Agilent E4980 LCR bridge, were performed in ceramics of rectangular shapes (3.35 mm × 2.40 mm and 1 mm in thickness). All measurements were performed under cooling at a constant rate of 2 K/min by using a Janis APD204E cryostat and a Lake Shore 331 temperature controller.

3. Results and discussion

The X-ray diffraction patterns and Rietveld refined results for the sintered BTO ceramic are shown in Fig. 1. The X-ray diffraction patterns were indexed by considering a tetragonal symmetry, typical for BTO single crystals [26]. In fact, the refinement model, which employed the P4/mmm space group and the Thompson–Cox–Hastings pseudo-Voigt profile function, which intrinsically consider internal strain effects on the diffraction patterns; resulted in satisfactory structural (a = 3.9967(1) and c = 4.0254(2)) and refinement (R_B = 1.50 and R_f = 0.82, R_{wp} = 9.86, and χ^2 = 7.9) parameters that attest this theoretical approach as adequate for describing the sample structure. Previous ferroelectric characterizations performed in these high-densified nanostructured BTO ceramics (98% of the theoretical density and grain sizes distribution centered at 500 nm) were recently reported [24] and a typical ferroelectric behavior, with saturation polarization close to BTO single-crystals, and a low remnant polarization typical of nanostructured ferroelectric compounds, was observed [24]. It is worth noting that these BTO ceramics, composed by morphologically symmetric

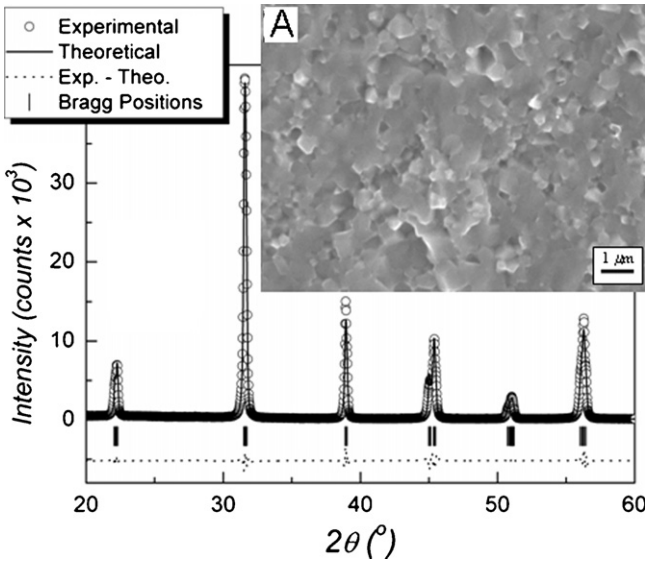

Fig. 1. (a) X-ray diffraction patterns (*P4/mmm* space group) and Rietveld refinement results for the nanostructured tetragonal $BaTiO_3$ ceramic. Inset A: fractured surface scanning electron microscopic image.