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Intrinsic and extrinsic effects near orthorhombic-tetragonal phase transition in barium titanate ceramics doped with small amounts of zirconium

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ABSTRACT

Pure BT and BT doped with 1 and 2 mol% Zr, with orthorhombic-tetragonal (O-T) phase transitions near room temperature were prepared, with different grain sizes, by conventional ceramic method, at various sintering temperatures. Intrinsic and extrinsic effects of Zr addition on structural, dielectric, piezoelectric and ferroelectric properties of BT ceramics, near O-T phase transition were studied. In coarse grained ceramics, the intrinsic effects manifested in low field measurements (dielectric and piezoelectric constants), were reduced by Zr addition, while the extrinsic effects which control the high field response (remanent polarization and coercive field) were significantly enhanced. Instead, in fine grains ceramics, of either pure or doped BT, the extrinsic effects related to increased domain wall and grain boundaries density were dominant in both low and high field measurements, overlapping Zr effects. The results were explained in terms of crystal anisotropy correlated with grain size effects.

1. Introduction

Barium titanate (BT) is a perovskite ferroelectric, well known among lead free materials. It was, extensively used in many applications as positive temperature coefficient thermistors, multilayer ceramic capacitors, pyroelectric sensors, phase shifters, tunable filters. Despite being one of the first developed piezoelectric ceramics of practical interest, barium titanate was ignored for a long time in piezoelectric applications, because of its relatively low Curie temperature ($T_c < 130$ °C) [1,2] and reduced performances [3] compared to those of lead based materials, recognized for their remarkable piezoelectric properties [2,4]. However, the present demand for environmental friendly materials, revived the interest for BT, which seems to have very promising perspectives, as it results from the recent achievements reported on high density pure BT ceramics with fine grains, obtained in special sintering conditions [5–7]. They showed excellent dielectric and piezoelectric performances, explained by the relationship between the nanosized ferroelectric domains and piezoelectric properties [8]. Besides, the use of dopants was another effective approach for improving material performances. One of the most explored was zirconium as an isovalent substitute for titanium ion. Zirconium shifts the polymorphic phase transitions to higher temperatures and decreases the Curie point as well. For higher doping levels (more than 10 mol%), Zr induces a relaxor behaviour in BT, extensively investigated [9–11]. Instead, the ferroelectric and piezoelectric properties, maintained for lower doping levels, were less studied [12,13]. In this work we used only 1 and 2 mol% Zr additions, which preserve the ferroelectric behaviour of BT and induce only a minor decrease of Tc. Furthermore, such small Zr doping levels shift the orthorhombic-tetragonal (O-T) phase transition near room temperature, resulting in increasing number of polarization orientations in the vicinity of this transition, which are supposed to improve the piezoelectric, ferroelectric and dielectric properties of BT ceramics. Besides, near the phase transition, material becomes dielectrically softer due to the flattening of the free energy [14]. This facilitates polarization rotation (tilt), the dominant field response of a “rotator” ferroelectric such as BT [15], which also enhances the piezoelectric and dielectric response. In this work, we studied the intrinsic and extrinsic effects of Zr addition on structural, dielectric, piezoelectric and ferroelectric properties of BT ceramics, near O-T phase transition. The results were discussed in terms of crystal anisotropy correlated with grain size effects.

2. Experimental procedure

BT and BT doped with 1 and 2 mol% Zr, denoted BZT1 and BZT2, respectively were prepared by conventional ceramic method. The raw

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materials: TiO_2, ZrO_2 and $BaCO_3$ were mixed 2 h, in methanol, using a planetary ball mill, with agate vessels, with a rotation speed of 250 rot/min. The dried homogeneous mixture was calcined 2 h at 1100 °C, for the solid state reaction synthesis, followed by milling at the same rotation speed, for 2 h. The calcined powders were dried and mixed with a binder (2 wt% polyvinyl alcohol) and then compacted into disk pellets, at 200 MPa, in a steel die. The pressed disks, of 12 mm in diameter and 3 mm thickness, were sintered in alumina crucibles, following one or two sintering steps. Different sintering schedules were used, with heating rates between 6 and 20 °C/min, first step higher sintering temperatures (HT) of 1400–1500 °C, with 1–60 min dwell times and second step lower temperatures (LT) of 1200–1300 °C, with dwell times of 3–10 h.

The ceramic disks were mechanically polished, to about 1 mm thickness and coated with silver paste electrodes, cured for 1 h at 200 °C. The samples were poled under 3 kV/mm DC field, in a silicon oil bath, for 10–20 min at the O-T transition temperature, as well as above Tc, maintaining the field during sample cooling. The dielectric and electromechanical properties of sintered ceramic samples were measured 24 h after poling, using an AGILENT 4294 A Impedance Analyzer (Agilent Technologies, Santa Clara, CA). The parallel capacitance and the dissipation factor were measured in vacuum of $5.4 \cdot 10^{-6}$ bar, in the temperature range of −250 and +200 °C, at different frequencies between 1 and 100 kHz. The dielectric constant was calculated using the measured capacitance and the geometry of the samples. Radial electromechanical coupling factor and the transverse piezoelectric coefficient d_{31} were obtained by resonance-antiresonance method. The mechanical quality factor of the radial mode was evaluated using the resonance band of the admittance spectra provided by the impedance analyzer [16]. The ferroelectric hysteresis loops (polarization vs. electric field) were registered with a Premier II ferroelectric test system (Radiant Technologies, Albuquerque NM, USA). The crystalline structure was investigated by X-ray diffraction (XRD), using a D8 ADVANCE X-ray diffractometer (BRUKER-AXS GmbH, Germany) with Ni filtered Cu radiation. A certified corundum sample (NIST SRM 1976) was used as a reference to assess the instrumental function. The sample displacement parameter was refined during the fitting of the lattice constants for each sample. The density was determined by Archimedes method. The ceramic morphology was revealed by using an EVO 50 scanning electron microscope (CARL ZEISS, Inc., Thornwood, NY).

3. Results and discussion

Different sintering schedules were used in order to obtain ceramics with a variety of grain sizes from 1 to 2 μm, or less, to 20–60 μm. The most representative sintering procedures were included in Table 1. We focused on two categories of ceramics with: i) coarse grains, of more than 20 μm and ii) fine graines of 1–2 μm, for which the grain size effects have distinct contributions (significantly higher in the last category) [17–19]. The experimental densities represented 95–98% of the theoretical densities, for all samples.

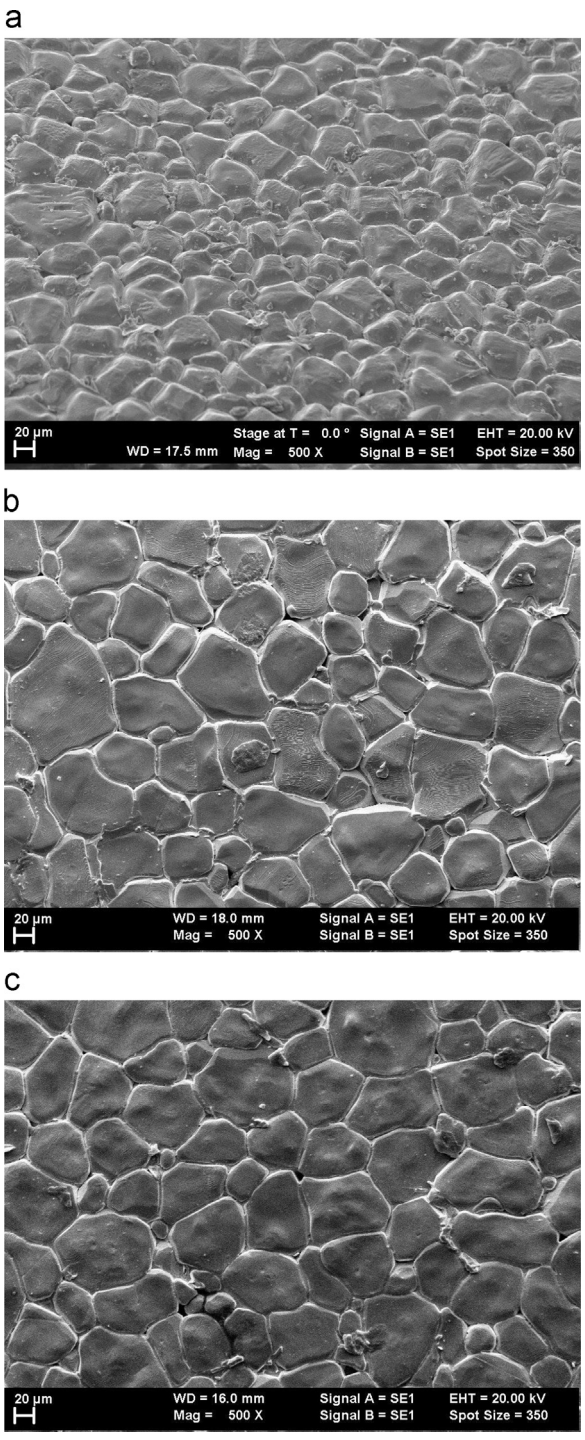

Fig. 1. SEM micrographs on unpolished surfaces of coarse grained (a) BT, (b) BZT1 and (c) BZT2 ceramics.

Table 1
Sintering schedules and resulting grain sizes.

Heating rate (°C/min)	6	6	20	9	9	16	20	20	20
HT (°C)	–	–	1300	1400	1400	1400	1400	1450	1500
HT dwell time (min)	–	–	1	20	20	5	30	30	30
LT (°C)	1200	1250	1200	1300	1300	1200	–	–	–
LT dwell time (h)	10	10	4	3	4	4	–	–	–
BT grain size (μm)	2–5	2–5 and 10–20 (rare)	≤1	20–40	40–50	5–20	–	–	–
BZT1 grain size (μm)	≤1 and 2–5	1–2 and 5–10 (rare)	≤1	20–60	40–60	30–50	–	–	–
BZT2 grain size (μm)	≤1	≤1	≤1	40–60	40–60	30–50	10–30	10–30	10–40