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Structure–microstructure–property relationships in lead-free BCTZ piezoceramics processed by conventional sintering and spark plasma sintering

Feres Benabdallah[a,b,c,*], Catherine Elissalde[b,c], U.-Chan Chung Seu[b,c], Dominique Michau[b,c], Angeline Poulon-Quintin[b,c], Marion Gayot[d], Pascale Garreta[d], Hamadi Khemakhem[a], Mario Maglione[b,c]

[a] Laboratoire des Matériaux Ferroélectriques, Faculté des Sciences de Sfax,Université de Sfax, BP802, 3018 Sfax, Tunisia
[b] CNRS, ICMCB, UPR 9048, F-33600 Pessac, France
[c] Université Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France
[d] PLACAMAT, UMS 3626CNRS-Université Bordeaux, F-33600 Pessac, France

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ABSTRACT

Lead-free piezoelectric ceramics belonging to the pseudo-binary system $(1-x)BaTi_{0.8}Zr_{0.2}O_3$-$x$ $Ba_{0.7}Ca_{0.3}TiO_3$(BCTZ, $x=0.32$ and 0.5) were prepared using conventional sintering and spark plasma sintering. This comparative study shows how the macroscopic properties of ferroelectric BCTZ perovskites are affected when the grain size is decreased. The crystallographic structure and the microstructural characteristics are thoroughly investigated for ceramic samples obtained by both sintering methods. We clearly demonstrate that the dielectric, piezoelectric, pyroelectric and ferroelectric properties in SPS ceramics are strongly affected by the grain size and the structural defects leading to local strain fields which undermine the polarisation flexibility. This confirms that the critical compositions showing remarkably large piezoelectric coefficients are extremely sensitive to external and internal stresses.

1. Introduction

For more than half a century, lead-based piezoelectrics such as $PbZr_{1-x}Ti_xO_3$(PZT), Pb $(Mg_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$ (PMN-PT) and $Pb(Zn_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$ (PZN-PT) have dominated the area of actuator, sensor and transducer technology. These lead-based materials are commonly used with compositions near the morphotropic phase boundary (MPB) where the crystal structure changes abruptly and the electro-mechanical properties are maximized [1–4]. Over the last decade, environmental concerns have been strongly driving the need to replace the lead-based perovskites by equivalent or better performance lead-free piezoelectric materials [5,6]. Thus, two different approaches have been considered. The first one, the so-called 'compositional engineering approach', focuses on the enhancement of electro-mechanical properties by selecting compositions close to a region with structural instabilities such as polymorphic phase transition (PPT) or MPB [7–10]. The coexistence of different competing phases with equivalent free energies allows a 'softening' of the crystal lattice and an increased alignment of ferroelectric domains during poling (several equivalent polarization orientations at the nanoscale). This gives rise to high piezoelectric effect through polarization rotation or polarization extension mechanisms [11]. The second approach is centered on the 'structurally engineered materials' by controlling the micro and/or nanoscale structure. It mainly relies on various structural engineering techniques such as grain size optimization, templated grain growth and domain engineering [4,12,13].

Few years ago, the first approach was successfully used to prepare novel perovskite-structured solid solutions $(1-x)BaTi_{0.8}Zr_{0.2}O_3$-$xBa_{0.7}Ca_{0.3}TiO_3$(BCTZ) with a surprisingly large electro-mechanical response surpassing that of the ultrasoft PZT-5H close to room temperature [14]. The unusual properties of the Pb-free pseudo-binary system were attributed to the vanishing polarization anisotropy near a phase convergence region (a nearly spherical degeneration of the free energy surface related to structural instabilities) [15]. Such discovery fostered many researchers to develop even-higher-performance $BaTiO_3$-based materials. Indeed, a modified lead-free piezoelectric BCTZ with higher Curie temperature T_c and colossal piezoelectric activity

* Corresponding author at: Laboratoire des Matériaux Ferroélectriques, Faculté des Sciences de Sfax,Université de Sfax, BP802, 3018 Sfax, Tunisia.
E-mail address: feresbenabdallah@yahoo.fr (F. Benabdallah).

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was designed by increasing the Curie temperature of the two end members in the phase diagram [16]. Moreover, <001> textured BCTZ ceramics (BCTZ50, $x = 0.5$) were synthesized by Ye et al. using templated-grain growth method. The obtained materials were shown to exhibit higher piezoelectric constants and larger electro-mechanical coupling factors compared to those of randomly oriented BCTZ ceramics whilst T_c revealed an increase with the template content [17].

In parallel to the extensive research of new lead free piezoelectrics, the current miniaturization trends in ceramic technology along with the growing consideration for production costs have compelled research efforts to process dense ferroelectric ceramics with both tailored grain sizes and optimal properties using non-conventional methods of synthesis (sol–gel, mechanosynthesis) and sintering such as hot pressing (HP) or spark plasma sintering (SPS). In the latter case, the sintering process allows obtaining high-density ceramics at lower temperatures and shorter processing times (typically a few minutes) compared to conventional sintering. As a result, grain coarsening can be limited. Interestingly, one can mention numerous achievements on the preparation of fine-grained ceramic materials ($BaTiO_3$, $Ba_{1-x}Sr_xTiO_3$, $BaTi_{1-x}Zr_xO_3$, $K_{0.5}Na_{0.5}NbO_3$(KNN), modified KNN, $(1-x)\,Bi_{0.5}Na_{0.5}TiO_3$-$x\,BaTiO_3$ (BNT-BT), ...). Detailed studies have been thus presented elucidating the relationships between the crystallographic structure/grain sizes/domain configurations and their ferroelectric/piezoelectric properties [18–24]. However, few available data were reported in the literature emphasizing such correlations in the BCTZ solid solutions, when the grain size is reduced [25,26].

Adjusting the grain size close to 1 μm in $BaTiO_3$ ceramics allows to enhance permittivity and piezoelectric coefficient by increasing domain wall density [27]. In addition, a controlled microstructure in terms of defects is also challenging regarding their impact on domain-wall contributions to the dielectric, elastic and piezoelectric properties. Such fine control of the microstructure is hardly achieved using conventionnal sintering as the high sintering temperature required to reach high density promotes grain growth and the long holding time can favor defects. SPS is now well recognized as a very efficient technique to obtain highly densified nanostructured ferroelectric ceramics and this fast consolidation process was largely used to probe the influence of size effects on properties. In this context, in depth investigations of BCTZ piezoceramics with selected compositions and controlled grain size using advanced sintering technique are still required for a better understanding of the relationships between structure, microstructure and functional properties. We propose a comparative study of BCTZ ceramics (compositions $x = 0.32$ and 0.5) processed by conventional sintering and SPS. The aim is to probe the impact of the microstructure on the dielectric, pyroelectric, ferroelectric and piezoelectric responses of BCTZ ceramics.

Structural defects induced by the SPS process were linked to a lower domain wall mobility which could explain the altered piezoelectric and ferroelectric performances of the BCTZ compositions sintered by SPS.

2. Experimental

The perovskite-structured BCTZ powders with a generic formula $(1-x)\,BaTi_{0.8}Zr_{0.2}O_3$-$x Ba_{0.7}Ca_{0.3}TiO_3$ ($x = 0.32$ and 0.5) were synthesized by conventional solid state reaction method using as starting chemicals, $BaCO_3$ (99.95%), $CaCO_3$ (99.5%), ZrO_2 (99.99%) and TiO_2 (99.9%). For each composition, the raw materials were weighed according to the stoichiometric formula and mixed by ball milling in alcohol using zirconia balls for 4 h. After being dried, the mixtures were calcinated in oxygen atmosphere at 1350 °C during 15 h, then ball milled again to break the agglomerates. Two sintering methods were used to obtain dense BCTZ ceramics with different grain sizes and morphologies. For spark plasma sintering, the powders were loaded in a cylindrical graphite die with an inner diameter of 10 mm and heated under vacuum using an SPS apparatus (Syntex Inc., SPS-515S). The rapid heating was achieved owing to a pulsed direct electric current traversing the die. The temperature was raised at 50–100 °C/min and kept at a constant value of 1300 °C for 10 min. Afterwards, the sample was cooled to 600 °C with a relatively low cooling rate of 35 °C/min and then, to room temperature by shutting down the power supply. A constant pressure of 90 MPa was applied along the *Z*-axis of the graphite die during the whole sintering process. Finally, the SPS-processed samples were annealed in oxygen at 900–1000 °C for 12 h in order to remove surface carbon contamination and to limit oxygen vacancies caused by the reducing conditions. For the conventional sintering, the powders were pressed into disks ($\Phi = 8$ mm, $e = 1$ mm) under a uniaxial pressure of 120 MPa and sintered at 1450 °C for 4 h under oxygen atmosphere.

Phase structure of the BCTZ powders and ceramics was identified by X-ray powder diffraction (XRD) using a PANalytical X'Pert MPD diffractometer with Cu Kα radiation of wavelength 1.54056 Å. The XRD patterns were recorded at room temperature with scan rates ranging from 0.02 to 0.008° and a counting time of 70 s/step. The microstructures of the ceramic samples were observed using a scanning electron microscope (SEM, JEOL 6360 A) and a transmission electron microscope (TEM-FEG, JEOL-JEM-2200FS with an acceleration voltage of 200 kV). Fractures of SPS ceramics (BCTZ32) were thermally etched at 1200 °C. The samples were introduced in the hot region of the tube furnace, kept at 1200 °C during 1 h and then quenched. BCTZ50 ceramics were chemically etched in HCL for 4 h. The grain size of the sintered ceramics was evaluated by linear intercept method on scanning electron microscopy micrographs. The average grain size was evaluated for each sample based on at least 100 grains. Thin foils for TEM were prepared by mechanical polishing to a thickness of 80 μm and argon ion-beam polishing using a 691 Gatan Precision argon Ion Polishing System (PIPS, 5 kV).

For electrical measurements, both sides of polished ceramic disks were sputter coated with gold electrodes. The temperature dependence of the dielectric constant and losses were measured at different frequencies ($10^2 - 10^5$ Hz) using an LCR meter (Wayne Kerr 4300) connected to a high-temperature tube furnace. The polarization–electric field (P–E) hysteresis loops were recorded at room temperature based on a standard Sawyer–Tower circuit. Samples for pyroelectric and piezoelectric measurements were poled under various DC electric fields (≈10–15 kV/cm) during cooling from the ferroelectric–non ferroelectric phase transition temperature down to the low-temperature region where a stable ferroelectric phase with rhombohedral symmetry was evidenced for both BCTZ compositions. The piezoelectric responses for the radial mode were determined at room temperature by the resonance–antiresonance method on the basis of IEEE standards [28]. The thermal variation of the pyroelectric current and the spontaneous polarization P_s was investigated for all samples by using a digital multimeter Keithley 2100.

3. Results and discussion

3.1. Microstructural characterizations

Scanning electron microscope (SEM) images of fracture surfaces illustrate the microstructural features of the BCTZ ceramics prepared by conventional and spark plasma sintering methods (Fig. 1a–f). All the samples are well densified with almost no