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Journal of the European Ceramic Society 34 (2014) 3661–3674

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Multiscale study of ferroelectric–relaxor crossover in $BaSn_xTi_{1-x}O_3$ ceramics

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Received 24 April 2014; received in revised form 30 May 2014; accepted 3 June 2014
Available online 5 July 2014

Abstract

A systematic study of $BaSn_xTi_{1-x}O_3$ solid solutions ($x = 0$–0.20) by a combined field-induced dielectric and ferroelectric analysis with Raman and PFM investigations was realized, in order to obtain new insights concerning the composition-induced modification of the structural phase transitions and ferroelectric–relaxor crossover induced by the increase of Sn addition. The ceramics prepared *via* solid state reaction and sintering at 1400 °C/4 h showed average tetragonal symmetry for $x \leq 0.15$ and cubic for $x = 0.20$. However, the dielectric and Raman analysis demonstrated that $x = 0.05$ and $x = 0.15$ are characterized by a coexistence of phases, which enhances their macroscopic properties (polarization for $x = 0.05$ and permittivity for $x = 0.15$). The domain structure shows a gradual modification when increasing Sn addition. No detectable domain structure has been found for $x \geq 0.15$. All the compositions show local $d_{33}(V)$ hysteresis loops at room temperature.

Keywords: Barium stannate titanate; Ferroelectric; Local hysteresis; PFM; Domains

1. Introduction

Barium titanate ($BaTiO_3$) is one of the most extensively studied perovskite (ABO_3) ferroelectric oxides, whose excellent dielectric and ferroelectric properties are largely exploited in various electronic devices such as capacitors, thermistors, transducers and nonvolatile memories in the microelectronic industry. Substitution of other ions at A, B or in both sites in the $BaTiO_3$ perovskite cells leads to remarkable changes of its functional characteristics. Relaxor character with improved dielectric performances for specific applications requirements *e.g.* higher material constants (permittivity, pyro- and piezoelectric constants), better thermal stability in a large temperature range and a diminished $P(E)$ and tunability $\varepsilon(E)$ hysteresis loops can be induced by isovalent substitution on Ti sites with elements such as: Zr,[1–4] Hf,[5,6] Ce,[7,8] or Sn.[9–17]

Barium stannate titanate $BaSn_xTi_{1-x}O_3$ (BSnT) represents one of the earliest prototype among $BaTiO_3$-based compounds with diffuse ferroelectric–paraelectric phase transition at high Sn additions.[9] This compound recently attracted attention due to its interesting dielectric relaxation properties[11–13] and its strong dielectric nonlinearity (tunability) which have high potential in microwave applications.[14,16,17] As in other

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http://dx.doi.org/10.1016/j.jeurceramsoc.2014.06.005
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$BaM_xTi_{1-x}O_3$ solid solutions, the room temperature permittivity and piezoelectric coefficient can be tailored to very high values for specific Sn substitutions, due to the shift of the ferroelectric–paraelectric phase transition toward lower temperatures when increasing the Sn addition and to overlapping of the rhombohedral–orthorhombic and orthorhombic–tetragonal structural phase transitions with the tetragonal-cubic one.[9,10,15] The high dielectric constant combined with low losses makes this material a valuable candidate for high permittivity applications, with similar performance as barium zirconate titanate.

From a fundamental point of view, the microscopic mechanism driving to the ferroelectric–relaxor crossover and its specific features, which are induced by the homovalent substitution on the Ti^{4+} site perovskite lattice of $BaTiO_3$-based solid solutions still needs to be clarified. Macroscopically, a similar behavior has been reported in all $BaM_xTi_{1-x}O_3$ compounds when increasing the substitution degree x: increase of the diffuse character of the ferroelectric–paraelectric phase transition toward the relaxor-like behavior; reduction of the ferroelectric character (toward slimmer $P(E)$, $\varepsilon(E)$ and $d_{33}(E)$ loops with almost zero coercivity); shift of the low-temperature structural phase transitions toward higher temperature values and a concurrent reducing of the temperature specific to the tetragonal-cubic (ferroelectric–paraelectric) one which results in a broad temperature and compositional range characterized by the coexistence of different crystalline phases. The microscopic mechanism driving these properties is related to the progressive reduction of ferroelectric interaction of long-range order due to the presence of local fluctuations[18] and to the loss in structural coherence correlation determined by the M substitution.[19,20] An atomistic picture of the ferroelectric-relaxor crossover with increasing the substitution degree was found for $BaZr_xTi_{1-x}O_3$. For this compound it was demonstrated that the degree of displacement correlation between Ti^{4+} ions is stronger and extends to larger distances for the ferroelectric state than for the relaxor ones and the overall off-centering behavior of Ti ion (responsible for the ferroelectric distortion and spontaneous polarization) changes from directional (in the ferroelectric state) to random displacements (in the relaxor state). Another characteristic of the ferroelectric–relaxor crossover is the transformation of the long range ferroelectric domains into short range order polar regions. These polar nanoregions (PNRs) are very stable against temperature and exist far above the Curie temperature range, even a few hundreds degrees higher, as observed by Raman spectroscopy.[8,16]

The ferroelectric–relaxor crossover has been mostly investigated at the macroscale, mainly in search for compositional ranges where the functional properties are enhanced. However, the ferro/piezoelectric properties are strongly related to the nature and mobility of domain walls. Local switching has been rarely checked in ferroelectric and relaxor compositions of the same system and most of the domain-related studies focused on tetragonal $BaTiO_3$ ceramics.[21,22] The domain structure in orthorhombic $BaZr_xTi_{1-x}O_3$ ceramics studied by optical investigation[23] was correlated with piezoelectric properties. The domain structure and local switching in some $BaZr_xTi_{1-x}O_3$ compositions with combined ferroelectric–relaxor behavior ($x=0.10$ and $x=0.18$) showed a few features which could be assigned to the increase of the relaxor character when increasing x.[24] For the specific case of $BaSn_xTi_{1-x}O_3$, an AFM study revealed mosaic-like domain structures for the relaxor compositions at high tin additions and the presence of PNRs whose dynamics was assigned to dielectric relaxation processes.[25] However, the as-grown domain structure as a function of composition was not clearly observed and local switching experiments have not been reported so far.

The present study is aimed to perform a multiscale investigation of the ferroelectric–relaxor crossover characteristics in $BaSn_xTi_{1-x}O_3$ ceramics by means of a combined dielectric, ferroelectric, Raman and AFM piezoresponse methods.

2. Sample preparation and experimental details

A series of ceramic samples with the composition $BaSn_xTi_{1-x}O_3$ ($x=0.05$, 0.10, 0.15 and 0.20) have been prepared by the solid state reaction, as described in detail in our previous study,[15] from p.a. grade oxides and carbonates: TiO_2 (Merck), SnO_2 (Merck) and $BaCO_3$ (Fluka), by a wet homogenization technique in iso-propanol. The initial mixtures were dried and shaped by uniaxial pressing at 160 MPa into pellets of 20 mm diameter and ∼3 mm thickness. After the pre-sintering thermal treatment performed in air at 1200 °C with 3 h plateau, the samples were finely grounded in an agate mortar, pressed again into pellets (of 13 mm diameter and ∼2 mm thickness) using an organic binder (PVA). These pellets were sintered in air at 1400 °C, with a heating rate of 5 °C/min and a soaking time of 4 h and then they were slowly cooled at the normal cooling rate of the furnace. By comparison with our previous study,[16] where microstructural and functional characteristics of ceramics sintered at 1300 °C/4 h were reported, in the present study a higher sintering temperature was employed, in order to produce dense ceramics with larger grains, more suitable for a PFM study. By comparison with our previous study,[15] a higher sintering temperature was employed (1400 °C) in order to produce dense ceramics with larger grains, to be more suitable for a PFM study.

X-ray diffraction (XRD) measurements at room temperature used to check the purity and formation of the perovskite phases were performed with a SHIMADZU XRD 6000 diffractometer using Ni-filtered CuKα radiation ($\lambda=1.5418$ Å) with a scan step increment of 0.02° and with a counting time of 1 s/step, for 2θ ranged between 20° and 80°. To estimate the structural characteristics, the same step increment, but with a counting time of 10 s/step, for 2θ ranged between 20° and 120° was used. The parameters to define the position, magnitude and shape of the individual peaks were obtained using the pattern fitting and profile analysis of the original X-ray 5.0 program. The lattice constants calculation is based on the least squares procedure (LSP) using the linear multiple regressions for several XRD lines, depending on the unit cell symmetry. To analyze the microstructure and to check the local chemical composition, a HITACHI S2600N scanning electron microscope coupled with energy dispersive X-ray spectroscopy (EDX) was employed.