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Investigation of $Ba_{1-x}Sr_xTiO_3$ ceramics prepared from powders synthesized by the modified Pechini route

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Abstract

$Ba_{1-x}Sr_xTiO_3$ ($x = 0$, 0.20, 0.25, 0.30 and 0.35) nanopowders were prepared by Pechini method from titanium isopropoxide, barium and strontium carbonates using citric acid as a chelating agent and ethylene glycol as an esterification agent. X-ray diffraction data show the formation of (Ba,Sr)TiO_3 solid solutions, free from secondary phases as $BaCO_3$ or Ti-rich oxides, when the polymeric precursors were calcined in air at 850 °C for 2 h. Ceramic pellets with relative density of 85–93% were obtained after sintering at 1350 °C for 3 h. High values of the dielectric constants (of ~1500–12,000), low losses at the room temperature and a shift of the ferro-para phase transition temperature in the range of 7–127 °C with x decreasing were found. Lower values of the Curie constant for higher x indicate the increase of the chemical and electrical local heterogeneity degree.

Keywords: Precursors-organic; Dielectric properties; Ferroelectric properties; $BaTiO_3$ and titanates; Perovskites

1. Introduction

The perovskite (Ba,Sr)TiO_3 (BST) is a intensively investigated ferroelectric due to its unique properties (high permittivity, resistivity and tunability), which makes it a promising candidate for electronic applications such as multilayer and voltage-tunable capacitors, infrared sensors, electrooptic devices and memories. The mentioned characteristics strongly depend on composition, raw materials, processing, microstructure, temperature, electric field, and frequency, so that, efforts on the BST synthesis are still in progress in order to improve its properties.

To achieve fine microstructure and high performance, it is necessary to start with preparing fine, stoichiometric and narrow size distribution powder. For this purpose, several wet chemical non-conventional methods as oxalate,[1] citrate,[2] sol–gel,[3] self-propagating high-temperature synthesis[4] and hydrothermal techniques,[5] were proposed as alternative approach at the dry mixed-oxides synthesis, which presents the inconvenience of the obtaining of inhomogeneous microstructure, because of the high temperatures of the solid state reactions.

Despite the disadvantage of the relatively long preparation time, the polymeric precursors method (PPM), mainly based on the Pechini-type process[6] is one of the more widely used for the preparation of pure mixed-oxides nanopowders, due to the low costs of precursors, low synthesis temperature and ionic homogeneity at molecular level. Although this powder synthesis method ensures a good reproducibility in the properties of the subsequent, pure $BaTiO_3$ ceramics,[7–10] only a few data related to BST compositions synthesized by PPM were reported.[11]

In this work, the structural and microstructural properties and mainly, the dielectric behavior of some $Ba_{1-x}Sr_xTiO_3$ ceramics obtained from powders synthesized via PPM were investigated.

2. Experimental

The modified Pechini method[6] was used for powders synthesis. Barium–strontium citrate solutions (prepared by dissolving appropriate amounts of $BaCO_3$ and $SrCO_3$

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in 0.4 M citric acid) were added to clear, transparent, yellowish solutions of titanium isopropoxide, ethylene glycol and citric acid. The molar ratio of the precursors was $Ba(Sr)CO_3:Ti(OC_3H_7)_4:C_6H_8O_7:C_2H_4O_2 = 1:1:2:20$. The resulted solutions, permanently stirred at ∼80 °C for 2 h, became increasingly viscous until clear, yellow (Ba,Sr,Ti) gels were formed. To promote polymerization the gels were heated at 135 °C for 11 h, when they were converted in dark-brown glassy resins. The (Ba,Sr,Ti) resins were lightly ground and calcined at 300 °C for 2 h in static air. Annealing at 850 °C for 2 h was carried out in order to obtain single phase $(Ba,Sr)TiO_3$ powders.

Ceramic samples were obtained by pressing the perovskite powders into pellets of 15 mm diameter, which were then sintered in air at temperatures of 1300 and 1350 °C for 3 h.

X-ray diffraction measurements at room temperature, used to investigate the purity of the perovskite phases were performed with a SHIMADZU XRD 6000 diffractometer using Ni-filtered Cu Kα radiation (λ = 1.5418 Å), with a scan step of 0.02° and a counting time of 1 s/step, for $2\theta \in 20$–80°. To estimate the structural characteristics a counting time of 10 s/step, for 2θ between 20° and 120° was used. 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.

TEM investigations were performed with a PHILIPS CM 120 microscope in order to determine the morphology and the particle average size of the $(Ba,Sr)TiO_3$ nanopowders.

A HITACHI S2600N scanning electron microscope coupled with EDX was used to analyse the microstructure and to check the chemical composition of the ceramic samples.

The electrical measurements were performed on parallel-plate capacitor configuration, by applying Pd–Ag electrodes on the polished surfaces of the sintered ceramic disks.

The $P(E)$ loops at room temperature were recorded under a sinusoidal waveform of amplitudes $E_0 = 1.5$–3 MV/m by using a modified Sawyer–Tower circuit. The complex impedance in the frequency domain 1–10^6 Hz and for temperatures below 200 °C was determined by using an impedance analyzer (Solartron, SI 1260).

3. Results and discussions

The X-ray diffraction patterns obtained for $Ba_{1-x}Sr_xTiO_3$ powders annealed at 850 °C/2 h and slowly cooled at room temperature show single-phase compositions for all the samples (Fig. 1). All the diffraction peaks are shifted towards higher diffraction angles, as strontium content increases. The TEM analyses revealed the obtaining of uniform particles, with an average size of ∼44 nm and an accentuated tendency to form aggregates or agglomerates (Fig. 2), irrespective of the strontium content.

The ceramic sample with $x = 0.20$, sintered at 1350 °C/2 h exhibits a well-densified, pore-free microstructure, with bimodal grain distribution, consisting of both polyhedral, faceted, larger grains (of ∼13 μm) and smaller grains of ∼5.3 μm (Fig. 3a). As strontium addition increases, the small grains fraction increases progressively, so that the ceramic with the highest Sr amount ($x = 0.35$) seems to be almost homogeneous as grain size (Fig. 3b), tending to a monomodal distribution, with an average size of ∼4.9 μm and presenting lower density and higher porosity. The increase of Sr content induces disturbance in neck growth, affecting the grain boundary movement. The as-resulted Kirkendall-type porosity hamper densification in the heterogeneous systems like $(Ba,Sr)TiO_3$ solid solutions, as compared with the pure $BaTiO_3$. The lower grain growth rate and the formation of intergranular pores originate in the difference in diffusion rates between the two metallic species involved in the mixed crystals formation.[12]

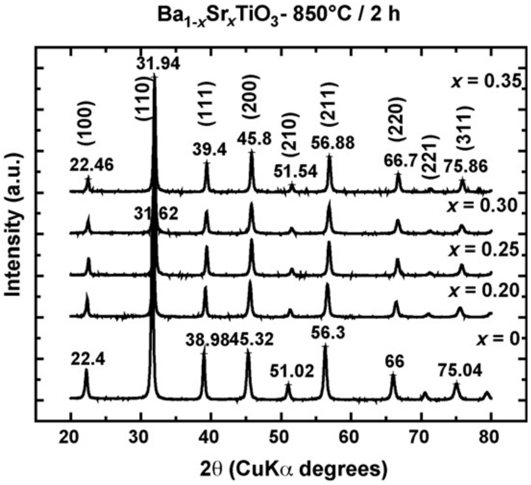

Fig. 1. X-ray diffraction patterns at room temperatures for $Ba_{1-x}Sr_xTiO_3$ nanopowders obtained after annealing at 850 °C for 2 h.

The structural parameters values calculated from XRD data and presented in Table 1 indicates that the tetragonality strongly decreases as strontium addition increases and therefore, the specimens with $x = 0.30$ and 0.35 present cubic symmetry.

Fig. 4 shows the $P(E)$ hysteresis loops obtained for the compositions $x = 0.25$ and 0.35 at room temperature. The switching characteristics are composition-dependent; by reduction of the coercitivity, polarization and area, they reflect the approaching of ferro-paraelectric phase transition at room temperature when x increases. The loops are rather tilted, with low rectangularity factor, due to the effect of some parameters as grain size and

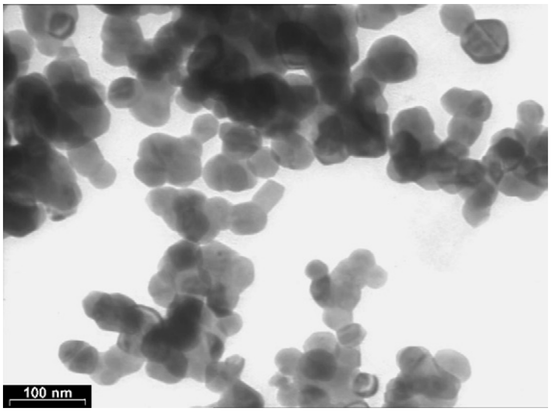

Fig. 2. Transmission electron micrograph of $Ba_{0.70}Sr_{0.30}TiO_3$ powder obtained after annealing at 850 °C for 2 h.

Table 1
Structural characteristics of (Ba,Sr)TiO_3 ceramics

	Composition [Sr]				
	$x=0$	$x=0.20$	$x=0.25$	$x=0.30$	$x=0.35$
Symmetry	Tetragonal	Tetragonal	Tetragonal	Cubic	Cubic
a (Å)	3.9981(11)	3.9782(4)	3.9608(7)	3.9542(9)	3.9523(6)
c (Å)	4.0282(32)	3.9917(10)	3.9737(16)	–	–
Tetragonality, c/a	1.0075(11)	1.0034(4)	1.0033(6)	1.0000(5)	1.0000(3)
Unit cell volume, V (Å^3)	64.39(9)	63.17(3)	62.34(5)	61.83(4)	61.74(3)

local compositional inhomogeneities originated in the random substitutional sites of the solute. The maximum available field $E_0 = 1.5$ MV/m was not enough to saturate the polarization in these ceramics. The loops for sample with $x = 0.35$ are very slim, with $P_r < 0.3\ \mu C/cm^2$ and $E_c < 1$ kV/cm, although still showing switching characteristics. This is a result of a field-induced ferroelectricity since at room temperature $Ba_{0.65}Sr_{0.35}TiO_3$ should be in its paraelectric state.[13]

High permittivity values (over 3000), were obtained at room temperature at $f = 105$ kHz, with a strong thermal variation induced by the proximity of the phase transitions (Fig. 5), due to the shift of tetragonal–cubic temperature towards lower values and orthorhombic–tetragonal transition towards higher temperatures with increasing x.[13,14] The $Ba_{0.70}Sr_{0.30}TiO_3$ and $Ba_{0.65}Sr_{0.35}TiO_3$ compositions have the transition below room temperature. These results are in good agreement with the structural parameters (Table 1). For all the BST ceramics, tan δ is less than 6% at this frequency, in the temperature range of 25–200 °C. All the compositions fully satisfy the Curie–Weiss law in the paraelectric region, with Curie constants in the range $(0.327–1.227) \times 10^5\ °C^{-1}$.

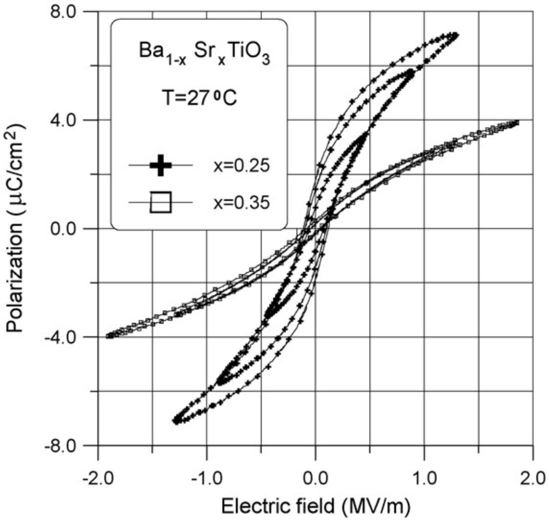

Fig. 4. $P(E)$ hysteresis loops for $Ba_{1-x}Sr_xTiO_3$ ($x = 0.25$ and 0.35) ceramics sintered at 1350 °C for 2 h.

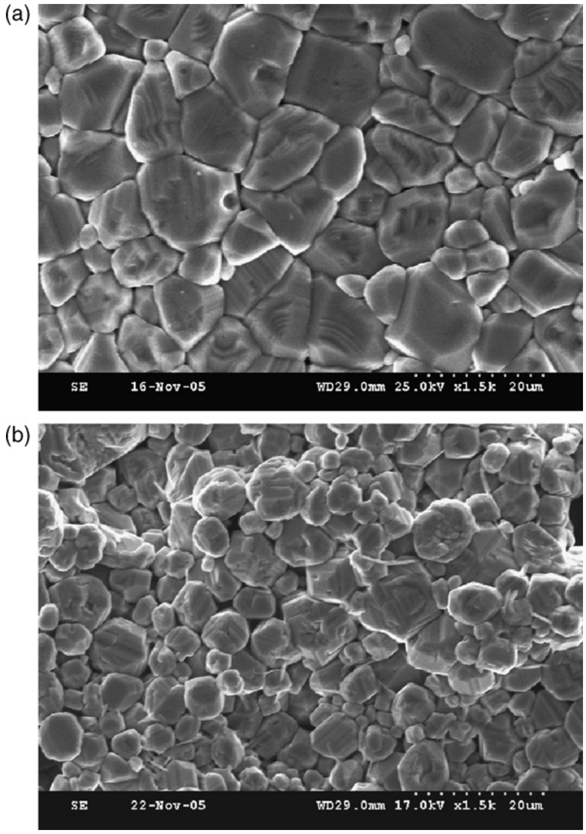

Fig. 3. Surface SEM images of: (a) $Ba_{0.80}Sr_{0.20}TiO_3$ and (b) $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics sintered at 1350 °C for 2 h.

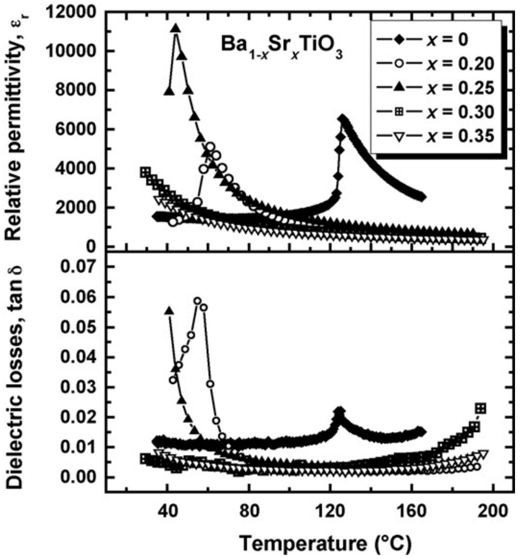

Fig. 5. Relative permittivity and dielectric losses vs. temperature at 105 kHz for $Ba_{1-x}Sr_xTiO_3$ ceramics sintered at 1350 °C for 2 h.

The sample corresponding to $x = 0.25$ presents excellent dielectric and ferroelectric properties related to its higher crystallinity, proved by the more intense and sharper diffraction peaks of this composition as compared with the diffraction peaks of the other BST ceramics. No significant dispersion in the ferroelectric phase as in relaxors was found by complex impedance analysis. The dielectric losses are lower than 2% and a bit higher at the ferro-paraelectric phase transition temperature (around 6% for $x = 0.25$ and 0.20).

4. Conclusions

Single phase (Ba,Sr)TiO_3 nanopowders, with a particle average size of ∼44 nm were prepared via polymeric precursors method. The ceramics obtained from the as-synthesized powders exhibited smaller grains, and lower densification and tetragonality, as strontium addition increased.

High values of the dielectric constants (of ∼1500–12,000), low losses at the room temperature and a shift of the ferro-para phase transition temperature in the range of 7–127 °C with x decreasing were found.

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