Dense, Fine-Grained Ba$_{1-x}$Sr$_x$TiO$_3$ Ceramics Prepared by the Combination of Mechanothesynthesized Nanopowders and Spark Plasma Sintering

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Ba$_{1-x}$Sr$_x$TiO$_3$ ($x = 0.025, 0.5, 0.75$, and $1$) nanocrystalline powders were prepared by mechanothesynthesis in a planetary mill, from stoichiometric mixtures of BaO, SrO, and TiO$_2$ at room temperature. Evolution during the mechanical treatment and subsequent annealings was investigated by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). Formation of the solid solution between BaTiO$_3$ and SrTiO$_3$ was observed in the whole range of compositions. The spark plasma sintering (SPS) technique was used to prepare dense ceramics. Densification occurred within a very short time (about 10 min). The combination of mechanothesynthesis and spark plasma sintering has been used for the first time to process ceramics of the Ba–Sr–Ti–O system with very high density and homogeneous microstructure, at a temperature $300–400$ °C lower than the conventional sintering of Ba$_{1-x}$Sr$_x$TiO$_3$ phases obtained by solid-state reaction. This approach allows grain growth to be controlled and opens the possibility of processing fully dense nanostructured Ba$_{1-x}$Sr$_x$TiO$_3$ ceramics. Dielectric permittivity as a function of temperature was characterized for a series of samples across the solid solution and confirmed that dense, fine-grained ceramics can be processed by this novel approach for all compositions. Ferroelectric hysteresis loops were recorded for BaTiO$_3$ ceramics with decreasing grain size. The variations of remanent polarization and coercive field are consistent with the transition from the lamellar 90° ferroelectric domain to grains with only 180° domains.

Introduction

Ferroelectric materials of barium titanate-based compositions with perovskite structure are extensively used in the electronic industry for multilayer ceramic capacitors, dielectric bolometers for infrared detection, dynamic random access memories (DRAM), and tunable capacitors for microwave technologies, all making use of their dielectric behavior around the ferroelectric–paraelectric transition. The transition of BaTiO$_3$ can be efficiently shifted toward room temperature by doping with different elements that substitute for Ba$^{2+}$ or Ti$^{4+}$ in the A and B sites, respectively. In addition to this, disorder broadens the phase transitions and so reduces the temperature dependence of the properties, which is necessary for the applications. Sr$^{2+}$ doping for Ba$^{2+}$ in BaTiO$_3$ is one of these substitutions that has attracted a lot of attention over the last years. The Curie point of BaTiO$_3$ is decreased by the substitution of strontium and coincides with room temperature for $x \approx 0.3$. Ferroelectric materials of this solid solution with good properties have been obtained and are under consideration mainly for tunable capacitors in microwave devices and pyroelectric imaging detectors. Thin films are the main candidates for replacing SiO$_2$–Si$_3$N$_4$ layers in very high density DRAMs.

These oxides are usually prepared by the conventional ceramic method, but high temperatures and long reaction times are required, which yield powders that are not suitable for the preparation of high-performance ceramics. This is so because very inhomogeneous particle sizes are obtained and a certain level of impurity content is difficult to avoid. Also, with the miniaturization of electronic devices, it became increasingly important to investigate the size effects on the properties when approaching the nanosize scales. To achieve this goal, powders with controlled stoichiometric and small and uniform particle size are required, and from these, nanostructured ceramics could be prepared. Ba$_{1-x}$Sr$_x$TiO$_3$ powders with small particle size can be prepared by various low-temperature methods, for example, coprecipitation, sol–gel synthesis, and the polymeric

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precursor method. However, most of these chemical routes require high-purity inorganic or organometallic reactants, which are more expensive than the widely available oxides and carbonates. Thus, alternative synthesis routes need to be developed that provide nanosized powder from more conventional reactants.

Mechanochemical activation techniques were developed for the synthesis of alloys and intermetallic compounds. More recently solid-state mechanochemistry has been used to prepare new oxides or to improve the properties of known functional materials. Mechanical activation usually produces disorder in the crystal and generation of defects that cause the decrease of the activation barrier for reaction. Mechanical treatment is a way to modify the conditions in which chemical reactions usually take place. During the high-energy milling, the particle size of the crystals is reduced, the homogeneity of the mixture is increased, and in most of the cases the solid becomes more reactive. Furthermore, the high reactivity and low particle size obtained facilitate the sintering process, thus making it possible to obtain high-density ceramics at low temperatures.

However, even if a small size powder is used, conventional sintering is unable to provide dense nanostructured ceramics due to the high temperatures still required for densification and the fact that the lowest grain size achievable by this technique remains about 0.5 μm. A technique that allows dense ceramics to be obtained at lower temperature is hot pressing (HP), where the pressure applied during the sintering process not only provides densification but also inhibits grain growth. Compared with the HP method, the spark plasma sintering (SPS) process permits high-density ceramics to be obtained under uniform heating at even lower temperatures and in much shorter processing times (typically a few minutes), a fact that further limits grain growth. This is because the rapid sintering of SPS allows the sample to skip the low-temperature regime, where the non-densifying mechanism (surface diffusion) is active, and proceed directly to the elevated temperature regime, where the densifying mechanisms (grain boundary and volume diffusion) are predominant. The SPS has been used to produce dense metals and ceramics for structural applications. Recently some researchers have applied this technique to produce electronic ceramics.

Experimental Section

About 3 g of stoichiometric mixtures of analytical grade BaO2, SrO, and TiO2 (anatase) for the Ba1−xSrTiO3 (x = 0, 0.25, 0.5, 0.75 and 1) was initially homogenized by hand in an agate mortar and activated in a planetary mill (Fritsch Pulverisette 6). The initial mixtures were placed in a stainless steel vessel with five steel balls 2 cm in diameter and 35 g in weight, the grinding bowl being rotated at 200 rpm. All mechanochemical treatments were carried out in air, for times up to 72 h.

For the sake of comparison, Ba1−xSrTiO3 powders were also synthesized by the traditional ceramic route. In that case, a stoichiometric BaCO3, SrCO3, and TiO2 mixture was treated at increasing temperatures from 500 up to 1250 °C, maintained at each temperature during different times, cooled by quenching, weighed, reground by hand in an agate mortar, and examined by X-ray diffraction.

Crystallographic evolution during mechanical activation and subsequent thermal treatment of the different mixtures was investigated by X-ray powder diffraction (XRD) with a Bruker AXS D8 Advance diffractometer between 5° and 60° (2θ), with 20 increments of 0.1° and counting time of 1.5 s per step. The Cu Kα doublet (λ = 0.15418 nm) was used in these X-ray experiments. For more detailed X-ray studies, a Philips X’pert diffractometer fitted with a primary Ge(111) monocrystal (Cu Kα1 radiation, λ = 0.15406 nm) was used. Slow scans with a step size of 0.02° and step time of 2 s were carried out. To obtain the lattice parameter and the crystallite size, least-squares methods and the Scherrer’s formula were applied to these data, respectively. Silicon (NIST standard reference material material 640b, a = 5.430940 ± 0.000035 Å for λCuKα1) was added as standard to reduce errors associated with lattice parameters calculations.

The mixtures were studied after milling and after thermal treatment by high-resolution electron microscopy. For these studies samples were crushed in an agate mortar and suspended in n-butanol. After ultrasonic dispersion, a droplet was deposited on a copper grid supporting a perforated carbon film. HRTEM images were recorded in a Philips CM200 FEG microscope. The micrographs were digitized for image processing and Fourier transformations were utilized to determine interplanar angles and spacings (Digital Micrograph). Lattice fringe spacings have been measured from the digital diffraction patterns (DDPs) by locating the maximum of intensity within the diffraction spots. Program Eje Z3D provided the information about the possible crystallographic orientations (zone axis) of a known crystal structure. Comparison between crystallographic data obtained by this application with that found experimentally from HRTEM micrographs after DDPs allows
the structure and the orientation of the material under analysis to be established. To confirm grain sizes obtained from XRD data, the particle size distribution of the mechanosynthesized samples was obtained by the Feret’s diameter from several HRTEM images of each sample.

Both mechanosynthesized powders and those obtained by the solid-state method \( \text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3 \) precursors [hereafter referred to as (m) and (s) precursors for the sintering step, respectively] were used to process ceramics. Sintering was accomplished in a vacuum in a SPS apparatus (Dr. Sinter 2050, Sumitomo Coal Mining Co. Ltd.). A cylindrical graphite die with an inner diameter of 8 mm was filled with the powder. When sintering by SPS, several parameters can be modified: the pressure used during the heating step \( P_h \), the final sintering temperature \( T_s \), the pressure applied during the isothermal sintering step \( P_i \), and the length of the isothermal treatment \( t_i \). A pulsed direct current was then passed through the pressure die to heat it up while the uniaxial pressure \( P_h (30-50 \text{ MPa}) \) was applied. The temperature was automatically raised to 600 °C, from which it was monitored and regulated by an optical pyrometer focused on the surface of the die. The temperature was then raised to the \( T_s (985-1400 \text{ °C}) \) at a heating rate of 100 °C·min\(^{-1}\) for all the samples, and when \( T_s \) was reached, a pressure \( P_i (50-140 \text{ MPa}) \) was applied. The soaking time \( t_i \) at the sintering conditions was varied between 0 and 8 min. The sintered ceramics were finally polished in order to eliminate the graphite off the surface. The SPS unit is provided with a dilatometer for recording the linear shrinkage of the sample as function of temperature and/or time. The ΔL values were corrected for the contribution of die expansion.

Ceramics were also processed by conventional sintering in air, at temperatures from 1200 to 1400 °C with a heating rate of 3 °C·min\(^{-1}\). Powders were shaped by uniaxial pressing at 210 kg·cm\(^{-2}\) as thin disks of 10 mm diameter and 2 mm thickness. These disks were then isostatically pressed at 2000 kg·cm\(^{-2}\), and finally, conventional-sintering was carried out on a Pt foil.

The density of the ceramics was obtained by the Archimedes’ method. Phases, crystallite size, and crystal structure were studied by XRD. Microstructure was characterized on fracture surfaces as well as on polished surfaces (up to 0.3 μm alumina) by scanning electron microscopy (SEM) and optical microscopy with JEOL JSM-6400 and JSM-6335F scanning electron microscopes and a Leitz Laborlux 12 ME S/ST optical apparatus, respectively.

Ceramic disks were thinned to 0.5 mm thickness and Ag electrodes were painted on the major faces and sintered at 650 °C for electrical characterization. The dependence of the dielectric permittivity on temperature at 10 frequencies, from 1 kHz to 1 MHz, was measured with a HP4192A impedance/gain phase analyzer, during a heating/cooling cycle with a 1 °C·min\(^{-1}\) rate. Details of the experimental setup can be found elsewhere. Ferroelectric hysteresis loops were recorded by current integration. Voltage sine waves of 0.1 Hz frequency and amplitudes up to 1000 V were applied by the combination of a synthesizer/function generator (Hewlett-Packard 3325B) and a bipolar operational power supply/amplifier (KEPCO BOP 1000M). Both the current integrator and the software for loop acquisition and analysis were developed in house. Loops were corrected (compensated) for linear polarization and conduction contributions as explained elsewhere.

**Results and Discussion**

**Synthesis and Structural Characterization of \( \text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3 \) (\( x = 0, 0.25, 0.5, 0.75, \) and 1).** A study concerning the mechanosynthesis of \( \text{SrTiO}_3 (x = 1 \text{ member}) \) was previously carried out by using a planetary mill, from a stoichiometric \( \text{SrO/ TiO}_2 \) mixture. Two steps were observed during the milling process: an initial diminution in particle size in the starting materials and a subsequent solid-state reaction in the activated mixture, which led to the formation of nanocrystalline perovskite after 72 h of grinding. When the different \( (1-x)\text{BaO}/x\text{SrO}/\text{TiO}_2 \) mixtures were mecha-nochemically activated in the planetary mill, similar results to those mentioned for the \( x = 1 \) mixture were obtained.

Figure 1a shows the XRD patterns of the different \( (1-x)\text{ BaO}/x\text{SrO}/\text{TiO}_2 \) mixtures activated during 72 h in a planetary mill, including the \( x = 1 \) sample, for the sake of comparison. For all compositions, a perovskite of the solid solution \( \text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3 \) was mechanosynthesized, which was isolated as a single phase after the mechanical treatment. In general, it can be said that higher Ba contents imply lower milling times for the perovskite to be mechanosynthesized. To investigate the crystallographic evolution of the samples activated during 72 h, thermal treatments at different temperatures were carried out. No other changes different from crystallite growth were observed by XRD. Figure 1b depicts the XRD patterns of the different activated samples annealed at 1200 °C for 12 h. Only for the case of \( \text{BaTiO}_3 \) (m), the formation of the tetragonal phase after the thermal treatment was observed when splittings became visible due to crystallite growth. According to previous works, the tetragonal phase was also expected for the case \( x = 0.25 \), but peak splittings were not observed for the phases here reported, probably due to their small particle size and subsequent peak broadening.

Table 1 summarizes the crystallite size and the lattice parameters for the perovskites after the milling and annealing treatments. Higher Ba contents resulted in the formation of larger particles. The cell parameter \( a \) of the solid solution

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decreases linearly with \( x \) according to linear expressions (Vegard’s law)

\[
a(\AA) = 4.001(8) - 0.104(3)x, \quad r = -0.9777 (0 \leq x \leq 1)
\]

for as-milled powders

\[
a(\AA) = 4.001(1) - 0.0957(9)x, \quad r = -0.9999 (0.25 \leq x \leq 1)
\]

for annealed powders

This variation is due to the difference between the ionic radius of Ba\(^{2+}\) \([r(\text{Ba}^{2+}) = 1.61 \text{ Å}]\) and Sr\(^{2+}\) \([r(\text{Sr}^{2+}) = 1.44 \text{ Å}]\).\(^{39}\)

\( \text{BaTiO}_3 (m) \) was also investigated by HRTEM. To consider the structural features as representative of the state of the sample, DDPs of different selected areas from several micrographs were studied. An example of a characteristic HRTEM micrograph is shown in Figure 2a, where a DDP of the selected particle is given. DDP is consistent with both the cubic and the tetragonal structure. These two polymorphs cannot be discerned by this technique. \( d \) spacings were assigned to \((11\bar{1})\) and \((1\bar{1}0)\) planes of the \( \text{BaTiO}_3 \) perovskite viewed in the direction of the \([11\bar{2}]\) zone axis.

Mechanosynthesized samples studied by HRTEM were constituted by well-defined crystalline particles (amorphous phases were not detected by this technique) the diameter of which was expected to be in good agreement with the value obtained from XRD data. Figure 2b shows the particle size distribution of the nanosized sample, obtained by the Feret’s diameter from an ensemble of more than 100 crystalline particles. The average diameter is 8.7 nm, consistent with the value obtained from XRD data (Table 1), as expected. The particle size distribution is broader for \( \text{BaTiO}_3 (m) \) than for \( \text{SrTiO}_3 (m) \), so maximum sizes up to 36 nm were found for the former, as compared with 17 nm for the latter.\(^{37}\)

**Ceramic Processing.** \( \text{BaTiO}_3 \) ceramics were first prepared by conventional sintering from both mechanosynthesized and solid-state reaction powders. XRD of the ceramics show that all of them are single phase. Parts a and b of Figure 3 depict the optical micrographs of the polished surfaces of the ceramics conventionally sintered at 1400 °C for 2 h from \( \text{BaTiO}_3 (s) \) and \( \text{BaTiO}_3 (m) \) precursors, respectively. Sintering at temperatures below 1400 °C resulted in ceramics with high porosity. It is clearly observed that the ceramic prepared from \( \text{BaTiO}_3 (m) \) has a higher density and a higher mechanical stability than the one obtained from \( \text{BaTiO}_3 (s) \), where pull-out and cracking occurred during polish.

To obtain dense ceramics at lower temperatures, spark plasma sintering was used as an alternative sintering method from both mechanosynthesized (m) and solid state (s) \( \text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3 \) precursors.

<table>
<thead>
<tr>
<th>phase</th>
<th>( x )</th>
<th>( a(\text{Å}) )</th>
<th>( \xi (\text{nm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{BaTiO}_3 )</td>
<td>0</td>
<td>3.99(1)</td>
<td>9</td>
</tr>
<tr>
<td>( \text{Ba}<em>{0.25}\text{Sr}</em>{0.75}\text{TiO}_3 )</td>
<td>0.25</td>
<td>3.983(5)</td>
<td>10</td>
</tr>
<tr>
<td>( \text{Ba}<em>{0.5}\text{Sr}</em>{0.5}\text{TiO}_3 )</td>
<td>0.5</td>
<td>3.958(8)</td>
<td>8</td>
</tr>
<tr>
<td>( \text{Ba}<em>{0.75}\text{Sr}</em>{0.25}\text{TiO}_3 )</td>
<td>0.75</td>
<td>3.924(9)</td>
<td>7</td>
</tr>
<tr>
<td>( \text{SrTiO}_3 )</td>
<td>1</td>
<td>3.89(3)</td>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>before annealing at 1200 °C/12 h</th>
<th>after annealing at 1200 °C/12 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a(\text{Å})/c(\text{Å}) )</td>
<td>( \xi (\text{nm}) )</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>4.001(3)/4.012(3)</td>
<td>40</td>
</tr>
<tr>
<td>3.9775(1)</td>
<td>43</td>
</tr>
<tr>
<td>3.9520(2)</td>
<td>35</td>
</tr>
<tr>
<td>3.9291(3)</td>
<td>36</td>
</tr>
<tr>
<td>3.9056(3)</td>
<td>34</td>
</tr>
</tbody>
</table>

All the ceramics prepared from \( \text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3 (s) \) precursors were sintered with \( P_h = 50 \text{ MPa}, P_t = 100 \text{ MPa}, t = 5 \text{ min} \), while \( T \) varied between 1200 and 1400 °C. The temperature dependence of the shrinkage for different samples is shown in Figure 4. In the case of \( \text{BaTiO}_3 (s) \), densification started at 1000 °C and was completed during the isothermal treatment at 1200 °C. It is obvious that a higher sintering temperature was required to densify \( \text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3 (s) \) \( (x = 0.25, 0.5, \text{ and } 0.75) \). For \( x = 0.25 \), shrinkage only started when the final temperature had been reached and the pressure was increased to 100 MPa. The density of these ceramics after SPS at 1200 and 1300 °C showed relatively low values and it was necessary to increase the sintering temperature to 1400 °C to prepare fully dense ceramics (Table 2). The behavior of the precursors corresponding to \( x = 0.5 \) and 0.75 was very similar to that described for \( x = 0.25 \). For the end member \( \text{SrTiO}_3 (s) \), the shrinkage began at 1150 °C, though

![Figure 2](image)

Figure 2. (a) HRTEM micrograph of the \( \text{BaTiO}_3 \) mechanosynthesized. Inset: DDP of the selected particle. (b) Particle size distribution from HRTEM images of \( \text{BaTiO}_3 \) mechanosynthesized.

it seemed to saturate at 1350 °C. However, further densification was obtained after several minutes under 100 MPa at 1400 °C.

The differences observed between the shrinkage curves of the end members and the members with \( x = 0.25, 0.5, \) and 0.75 are probably due to the different synthesis conditions for these precursors prepared by solid-state reaction. Higher temperatures were necessary for the intermediate compositions to form the solid solution as a single phase, which resulted in less reactive precursors because of larger particle sizes.

Table 2. Processing Conditions for the Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) Ceramics by SPS and Densities Obtained by the Archimedes Method

<table>
<thead>
<tr>
<th>precursor/synthesis method</th>
<th>( P_h ) (MPa)</th>
<th>( T_s ) (°C)</th>
<th>( P_i ) (MPa)</th>
<th>( t_i ) (min)</th>
<th>( \rho ) (g/cm(^3))</th>
<th>rel ( \rho ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO(_3)/solid state</td>
<td>50</td>
<td>1200</td>
<td>100</td>
<td>5</td>
<td>5.925</td>
<td>98.5</td>
</tr>
<tr>
<td>Ba(<em>{0.75})Sr(</em>{0.25})TiO(_3)/solid state</td>
<td>50</td>
<td>1200</td>
<td>100</td>
<td>5</td>
<td>4.800</td>
<td>82.6</td>
</tr>
<tr>
<td>Ba(<em>{0.5})Sr(</em>{0.5})TiO(_3)/solid state</td>
<td>50</td>
<td>1300</td>
<td>100</td>
<td>5</td>
<td>5.275</td>
<td>90.8</td>
</tr>
<tr>
<td>Ba(<em>{0.25})Sr(</em>{0.75})TiO(_3)/solid state</td>
<td>50</td>
<td>1400</td>
<td>100</td>
<td>5</td>
<td>5.651</td>
<td>97.2</td>
</tr>
<tr>
<td>SrTiO(_3)/solid state</td>
<td>50</td>
<td>1400</td>
<td>100</td>
<td>5</td>
<td>5.893</td>
<td>99.5</td>
</tr>
<tr>
<td>BaTiO(_3)/mechanosynthesis</td>
<td>50</td>
<td>1100</td>
<td>50</td>
<td>3</td>
<td>5.933</td>
<td>98.7</td>
</tr>
<tr>
<td>Ba(<em>{0.75})Sr(</em>{0.25})TiO(_3)/mechanosynthesis</td>
<td>50</td>
<td>1100</td>
<td>50</td>
<td>3</td>
<td>5.333</td>
<td>98.9</td>
</tr>
<tr>
<td>Ba(<em>{0.5})Sr(</em>{0.5})TiO(_3)/mechanosynthesis</td>
<td>50</td>
<td>1100</td>
<td>50</td>
<td>3</td>
<td>5.329</td>
<td>99.4</td>
</tr>
<tr>
<td>Ba(<em>{0.25})Sr(</em>{0.75})TiO(_3)/mechanosynthesis</td>
<td>50</td>
<td>1100</td>
<td>50</td>
<td>3</td>
<td>5.007</td>
<td>97.8</td>
</tr>
<tr>
<td>SrTiO(_3)/mechanosynthesis</td>
<td>50</td>
<td>1100</td>
<td>50</td>
<td>3</td>
<td>5.007</td>
<td>97.8</td>
</tr>
</tbody>
</table>

* \( P_h \) = heating pressure, \( P_i \) = isothermal step pressure, \( T_s \) = temperature, \( t_i \) = time, \( \rho \) = density.

Figure 3. Optical micrographs of the polished surfaces of BaTiO\(_3\) ceramics conventionally sintered at 1400 °C for 2 h from different precursors: (a) solid state synthesized and (b) mechanosynthesized.

Figure 4. Normalized shrinkage curves recorded during the SPS processing of the Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) ceramics from the solid-state synthesized precursors. (SPS conditions \( P_h = 50 \text{ MPa}, P_i = 100 \text{ MPa}, t_i = 5 \text{ min}, T_s \) varied between 1200 and 1400 °C).

Figure 5. Optical micrographs of the polished surfaces of ceramics processed by SPS under different conditions from solid-state prepared precursors: (a) BaTiO\(_3\) (\( P_h = 50 \text{ MPa}, P_i = 100 \text{ MPa}, t_i = 5 \text{ min} \)), (b) Ba\(_{0.75}\)Sr\(_{0.25}\)TiO\(_3\) (\( P_h = 50 \text{ MPa}, P_i = 100 \text{ MPa}, t_i = 5 \text{ min} \)), (c) Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) (\( P_h = 50 \text{ MPa}, P_i = 100 \text{ MPa}, t_i = 5 \text{ min} \)), and (d) SrTiO\(_3\) (\( P_h = 50 \text{ MPa}, P_i = 100 \text{ MPa}, t_i = 5 \text{ min} \)).
to $x = 0.25$, while the density of the Ba$_{0.75}$Sr$_{0.25}$TiO$_3$ ceramic prepared at 1400 °C is lower than that of the SrTiO$_3$ ceramic prepared under the same conditions. All these results are in good agreement with the Archimedes data collected in Table 2 and also with the shrinkage curves. As a result, the density of the ceramics is improved, and the processing time is significantly reduced by using SPS on a solid-state precursor. However, the sintering temperature was not significantly reduced for all compositions except for BaTiO$_3$.

To reduce the sintering temperature and to control grain growth and obtain more homogeneous microstructures, nanocrystalline Ba$_{1-x}$Sr$_x$TiO$_3$ precursors were employed for the SPS process. All the sintering conditions used yielded densities corresponding to 98–100% of the theoretical values, even for temperatures as low as 985 °C (Table 2).

When the in-situ shrinkage curves of the solid-state precursors (Figure 4) are compared with the curves of the nanosized precursors (Figure 6), it can be noted that the shrinkage started at a lower temperature with the latter powders than it does with the former. This difference can be interpreted in terms of the higher reactivity and lower particle size of the mechanosynthesized precursor.

The combination of mechanosynthesis and SPS produced single phase and fully dense ceramics of the solid solution Ba$_{1-x}$Sr$_x$TiO$_3$ at reduced processing temperatures for all studied compositions. Moreover, densification took place in a few minutes, demonstrating that synergy occurs by the combination of SPS process and mechanosynthesized powders. Negligible porosity was observed on the polished surfaces in agreement with the density values obtained by Archimedes’ method (> 97.5%).

Figure 7 shows the SEM images of fracture surfaces of some of the BaTiO$_3$ ceramics prepared by SPS. The fracture shown in Figure 7a corresponds to a ceramic prepared at a temperature of 985 °C and a pressure of 140 MPa. A mixed inter/transgranular mode is observed, in which grains ranging from below 100 to 200 nm can be seen. The fracture of Figure 7b corresponds to a ceramic sintered at 1100 °C and a pressure of 100 MPa and is basically transgranular. A comparison between the two ceramics is not obvious, due to the different fracture modes, but some grain growth seems to have occurred when the SPS sintering temperature was increased from 985 to 1100 °C. In the case of the micrograph shown in Figure 7c, the use of a precursor with a very large particle size BaTiO$_3$(s) and the increase of the temperature

![Figure 6. Normalized shrinkage curves recorded during the SPS processing of the Ba$_{1-x}$Sr$_x$TiO$_3$ ceramics from mechanosynthesized precursors. (SPS conditions: $P_h = 50$ MPa, $T_i = 1100$ °C, $P_i = 100$ MPa, $t_i = 3$ min).](image-url)

![Figure 7. SEM micrographs of the BaTiO$_3$ ceramics processed by SPS from different precursors using different conditions: (a) BTm $P_h = 30$ MPa, $T_i = 985$ °C, $P_i = 140$ MPa, $t_i = 8$ min; (b) BTm $P_h = 50$ MPa, $T_i = 1100$ °C, $P_i = 100$ MPa, $t_i = 3$ min; and (c) BTs $P_h = 50$ MPa, $T_i = 1200$ °C, $P_i = 100$ MPa, $t_i = 5$ min.](image-url)
to 1200 °C resulted in a ceramic with a larger grain size of about 2 μm. Nevertheless, this value is still significantly lower than the one observed in a ceramic obtained from this precursor by conventional sintering (about 10 μm).

All these results clearly show that the combination of mechanosynthesis and spark plasma sintering is an effective means of obtaining fully dense, very fine grained ceramics that cannot be obtained by the separate use of the two techniques.

**Electrical Characterization.** The dielectric properties of the fully dense Ba$_{1-x}$Sr$_x$TiO$_3$ ceramics prepared by the combination of mechanosynthesis and spark plasma sintering were investigated. A first series of Ba$_{1-x}$Sr$_x$TiO$_3$ samples with variable x sintered under the conditions $P_h = 50$ MPa, $T_i = 1100$ °C, $P_i = 100$ MPa, $t_i = 3$ min and (b) two BaTiO$_3$ samples, one prepared under the condition above-mentioned and other prepared by SPS using the conditions $P_h = 50$ MPa, $T_i = 1300$ °C, $P_i = 50$ MPa, $t_i = 3$ min.

In Figure 8a, the dielectric anomaly associated with the ferroelectric—paraelectric transition of BaTiO$_3$ is observed at 105 °C. For Ba$_{1-x}$Sr$_x$TiO$_3$ ceramics with $x > 0$, no anomaly is observed between 40 and 200 °C, but the negative derivative with the temperature for samples with $x > 0$ indicates the existence of a maximum at lower temperature. The magnitude of this negative derivative decreases when the strontium content increases, indicating that the phase transition occurs at decreasing temperatures, as expected. SrTiO$_3$ is an incipient ferroelectric for which an anomaly is not observed down to temperatures approaching 0 K.

The diminution of grain size for BaTiO$_3$ ceramics causes the increase of the permittivity in the ferroelectric phase; the reduction of the temperature of the ferroelectric—paraelectric phase transition, from 110 °C for the ceramic sintered at 1300 °C to 105 °C for the one prepared at a lower temperature; and the broadening of the anomaly (Figure 8b).

The dielectric properties of bulk ferroelectric materials result from the sum of the intrinsic single-crystal response of the system and extrinsic effects, like those associated with the dynamic of the ferroelectric domains and defects. When the behavior of the two BaTiO$_3$ samples is compared, it can be observed that grain size diminution causes a decrease of the temperature of the cubic to tetragonal transition. This transition is accompanied by a spontaneous strain and a small volume increase. For single crystals, this strain can be developed without stress generation, but in the case of the ceramics, where the grains are constrained, the volume change causes internal stresses to develop, which are minimized by the formation of 90° twins. Domain twinning in ferroelectric ceramics is dependent on grain size, so a banded lamellar structure relieves stress in three dimensions for coarse-grained ceramics. On fine-grained ceramics (<10 μm), however, a simple lamellar structure only allows two-dimensional stress relief. For even finer grained samples, 90° domains cannot be formed. A threshold of 40 nm has been estimated from energy considerations for the disappearance of 90° domain for the case of BaTiO$_3$. However, experimental results indicate that this threshold is around 0.4 μm. Though highly stressed, the material is still ferroelectric below the threshold, and switching occurs only by 180° domain wall nucleation and growth. Ferroelectric switching has been observed down to 50 nm. The shifting of the phase transition temperature as well as the anomaly broadening and the increase of permittivity for BaTiO$_3$ very fine grained ceramics are the consequence of the increasing internal stress developed when the grain size is decreased.

Ferroelectric hysteresis loops for the two BaTiO$_3$ ceramics with decreasing grain size are shown in Figure 9. Both samples show ferroelectric behavior, coercive electric field ($E_c$), and a remanent polarization ($P_r$) that is higher for the ceramic processed at a higher temperature. This is consistent with the behavior for the two BaTiO$_3$ ceramics with different grain sizes is depicted in Figure 8b.

![Figure 8. Temperature dependence of the permittivity of (a) Ba$_{1-x}$Sr$_x$TiO$_3$ ceramics processed from mechanosynthesized precursors by SPS ($P_h = 50$ MPa, $T_i = 1100$ °C, $P_i = 100$ MPa, $t_i = 3$ min) and (b) two BaTiO$_3$ samples, one prepared under the condition above-mentioned and other prepared by SPS using the conditions $P_h = 50$ MPa, $T_i = 1300$ °C, $P_i = 50$ MPa, $t_i = 3$ min.](image-url)
with a transition from a 90° lamellar domain structure to one without 90° domains, for which polarization switching occurs by 180° domain wall nucleation and growth. Remanent polarization must be higher for the former case as a consequence of the presence of 90° walls that are moved by the electric field. On the other hand, these walls are more difficult to move than 180° walls are, and thus the coercive field is also higher.

This is further supported by the good agreement between the ferroelectric parameters of the ceramic sintered at 1300 °C (P_R = 4.9 μC cm⁻² and E_C = 0.8 kV mm⁻¹) and those of a typical BaTiO₃ ceramic with the 90° lamellar domain structure reported by Arlt (P_R ~ 4 μC cm⁻² and E_C ~ 1 kV mm⁻¹).  

It is also worth comparing the electrical properties of the ceramics here reported with similar (in grain size) samples from the literature. BaTiO₃ ceramics with grain size in the range 0.05–0.3 μm have been processed by the combination of a chemical aqueous method and SPS. These samples presented a dielectric permittivity at 70 °C of 2200 and 1680ε₀, a Curie temperature of 118 and 105 °C, and a permittivity at T_C of 3200 and 1800ε₀, for grain sizes of 0.3 and 0.1 μm, respectively. These are values comparable with those of the ceramic sintered at 1100 °C here reported: a permittivity at 70 °C of 1470ε₀, a Curie temperature of 105 °C, and a permittivity at T_C of 1900ε₀. Ba₀.₆Sr₀.₄TiO₃ ceramics have been processed by SPS from BaTiO₃ and SrTiO₃ commercial powders. Unfortunately, they presented a bimodal grain size distribution with grains as high as 3 μm, so a direct comparison with the ceramics here reported is not possible.  

Conclusions

The mechanochemical activation of (1 - x)BaO₂/ₓSrO/ 
TiO₂ stoichiometric mixtures in a steel planetary mill led to the mechanosynthesis of nanosized particles of all the members of the Ba₁₋ₓSrₓTiO₃ solid solution.

The use of the very reactive precursors obtained by mechanosynthesis facilitates the sintering process. Despite this fact, still too high temperatures are necessary for achieving high-density ceramics from these precursors, and very fine grained samples cannot be obtained by conventional sintering. Spark plasma sintering has been applied as alternative method to overcome this problem.

By the combination of mechanosynthesis and spark plasma sintering, applied for the first time to this system, fully dense Ba₁₋ₓSrₓTiO₃ ceramics were obtained at much lower temperature (as low as 985 °C) in shorter sintering time (a few minutes) and so with a much finer grain size. By controlling SPS conditions, dense homogeneous microstructures with a grain size as low as 100–200 nm were obtained.

The study of the dielectric properties of Ba₁₋ₓSrₓTiO₃ ceramics confirmed the viability of this approach to obtain fully dense ceramics all across the solid solution range. The possibility of studying size effects by characterizing the dielectric and ferroelectric properties of BaTiO₃ ceramics so prepared was explored. Variations of remanent polarization and coercitive field observed are consistent with the transition from a 90° lamellar domain structure to one without 90° domains when ceramics are processed under SPS conditions, leading to decreasing grain size, and were characterized.

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