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$BaTiO_3$ devices doped with Zr using mechanical alloying

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Abstract

The purpose of this work was to compare the microstructure and electrical characteristics of $BaTiO_3$ devices doped with Zr for conventional fabrication and for mechanical alloying (MA). The sintered samples fabricated with MA powder showed better ZrO_2 dissolution and smaller grain sizes than the conventional samples. Lower values of loss factor and higher resistivities were observed in devices fabricated with MA powders. When the ZrO_2 concentration increases, the resistivity and the loss factor increase while the dielectric constant decreases. These effects are explained in terms of grain size reduction and lattice distortion.

Keywords: Ferroelectrics; Barium titanate; Mechanical alloying

1. Introduction

$BaTiO_3$ is commonly used with several additives. One of these substances, ZrO_2, is used in commercial formulations such as Z5U or NPO capacitors [1]. However, ZrO_2 is difficult to diffuse into the $BaTiO_3$ lattice which means high temperatures and long dwell times in the furnace during processing. It has been shown by our group [2] that using high energy milling it is possible to dissolve ZrO_2 into $BaTiO_3$ lattice where the Zr^{4+} ion replaces the Ti^{4+} ion in the perovskite structure, in other words, a mechanical alloy can be fabricated. CO_2 has to be avoided in the atmosphere during mechanical alloying between $BaTiO_3$ and ZrO_2 otherwise $BaCO_3$ is formed instead of the solid solution [3]. Mechanical alloying is a process where an alloy is formed at room temperature by milling a mixture of powders in a high energy milling device such as shaking (SPEX), planetary or attritor mill [4,5]. Mixers and milling devices are common facilities in ceramic plants such as those where capacitors are fabricated, hence this kind of facilities might be used to produce solid solutions at room temperature.

The high energy milling produces particle size reduction and some micro-deformation in the $BaTiO_3$ particles [3]. On the other hand in the conventional process, the dissolution of ZrO_2 in $BaTiO_3$ is carried out by thermally activated diffusion. Once the conventionally alloyed powder is pressed and properly sintered, a core–shell structure is observed in the microstructure where the solid solution is formed in an external layer of the grains (shells) while an internal volume in the grain (core) remains relatively free of Zr^{4+} ions [6,7]. When the piece is cooled down, this core–shell structure in the grain leads to a complex stress configuration due to the difference in thermal expansion coefficients between the core and shell regions in such a way that the core presents a pseudocubic lattice due to compression stresses. The shell region of the grains is also distorted due to the solid solution formation [6,7].

2. Experimental

Commercial $BaTiO_3$ (Merck, 0.45 μm average size, Ba/Ti < 1) and ZrO_2 (Tosoh, TZ-0, 0.6 μm average size) powders were used. On one hand, mixtures of $BaTiO_3$ + 1, 2 and 3 wt.% of ZrO_2 were milled in a planetary mill (Fritch, Pulverissete 5.0) during 8 h using ZrO_2 balls and a nylamide container with Ar atmosphere. Using this procedure and X-ray diffraction analysis, our group has shown that the alloy is indeed formed. The details can be found elsewhere [3]. In addition, the powder mixtures of the same concentrations were just mixed in a polyethylene vial for 24 h with distilled water following the conventional procedure. Mechanically alloyed (MA) and conventionally prepared powders were isostatically pressed at 300 MPa (Autoclave Eng.) and sintered in a furnace (Carbolite) at 1300 °C for 1 h with, 10°/min as heating rate and 20°/min as cooling rate. The pieces were cylinders of 1 cm of diameter. From these pieces 1 mm thick discs were sliced by a low speed cutter. After conventional polishing and etching, the microstructure of the samples were observed in a scanning electron microscope (JEOL 6300) and the average grain size was determined by

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an image analyzer (Image-Pro). To fabricate the devices, silver contacts were deposited by evaporation on both sides of the discs. The diameter of the contacts was 5 mm. Silver paint was used to cold solder a copper electrode on the contacts. The whole device was immersed in a high resistance epoxy resin (Eseisa MPT-M3, Mexico). Electrical properties were measured by impedance spectroscopy (Solartron 1260). To determine the dielectric constant and the resistivity of the samples, an equivalent circuit constituted by a capacitor and a resistance in parallel was considered. The loss factor was taken from the θ versus frequency curve at 1 kHz.

3. Results and discussion

In Fig. 1 the microstructures of sintered samples of both, conventional and MA samples with 1, 2 and 3 wt.% ZrO_2, are compared. In case of the conventional samples, at 2 wt.% ZrO_2, abnormal growth is evident which is due to the non homogeneous distribution of ZrO_2 in the material. However, in case of MA samples (Fig. 1), the abnormal growth is present with 1 wt.% of ZrO_2 whereas the MA sample with 2 wt.% of ZrO_2 presents a homogeneous microstructure. Abnormal grain growth results in MA samples with apparently less ZrO_2 concentration as compare to the conventional case. This result could be due more efficient diffusion since the ZrO_2 was diffused both by milling and by the sintering, whereas in the conventional case, the diffusion takes place only during the sintering. To obtain a fine grain microstructure, in the conventional case, more than 2 wt.% of ZrO_2 is necessary while in the MA case small grain size is obtained with less than 2 wt.% of ZrO_2 (Fig. 1). Such results can be seen in Fig. 2 where the average grain sizes are presented. Figs. 1 and 2 suggest that in the conventional case, larger amount of ZrO_2 was not dissolved into $BaTiO_3$ as compared to the MA case. In Fig. 3 the grain growth at various sintering temperatures for the conventional and MA cases are compared. Between 1200 and 1300 °C the grain growth is lower in the case of the MA samples as compared to the conventional samples. However between 1300 and 1400 °C the grain growth

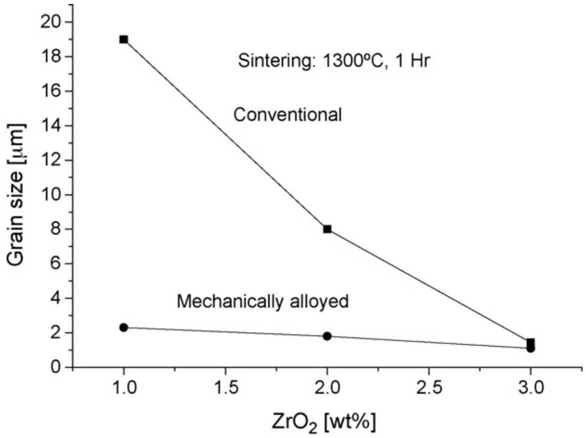

Fig. 2. Average grain size as a function of ZrO_2 concentration in conventional and mechanically alloyed samples sintered at 1300 °C during 1 h.

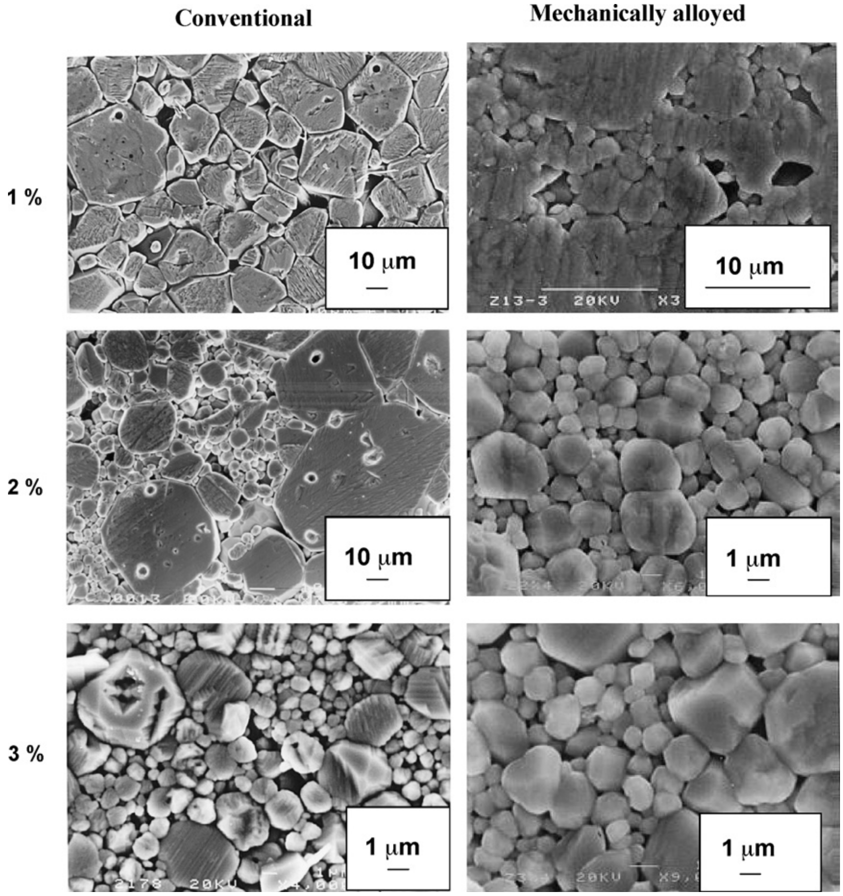

Fig. 1. Microstructures of the conventional and mechanically alloyed samples of $BaTiO_3$ with additions of 1, 2 and 3 wt.% ZrO_2, sintered at 1300 °C during 1 h.

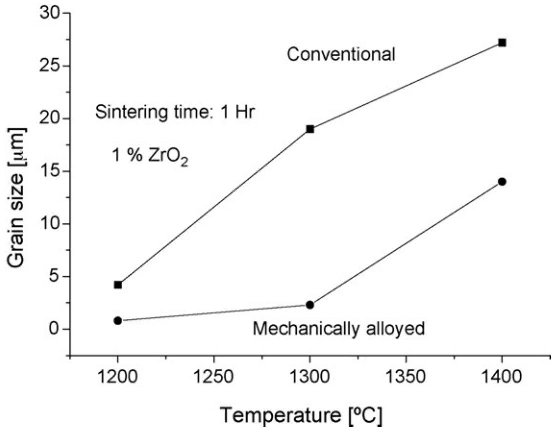

Fig. 3. Average grain size as a function of sintering temperature in conventional and mechanically alloyed $BaTiO_3$ + 1 wt.% ZrO_2 samples. The dwell time during sintering was 1 h.

becomes faster in the MA samples and it is comparable with the conventional samples because the small size in the grains implies great superficial area and therefore, high reactivity. Moreover it is well established that at 1300 °C occurs the third stage of sintering where grain growth is dominant [8].

An analysis of impedance spectroscopy results in the complex curves presented in Fig. 4. In the conventional as well as in MA samples the magnitude of the impedance increases when the ZrO_2 concentration is augmented. This relation suggests that the controlling parameter is the grain boundary because the effect of an increment in the ZrO_2 content results in an additional grain size reduction. Moreover, the MA samples show the highest impedances since these samples have the smallest grain sizes. This tendency can also be observed comparing the resistivity values of the samples shown in Table 1. In all cases the impedance curves are constituted by only one semicircle which implies that there is one dominant mechanism. Due to these reasons, such a mechanism seems to occur at the grain boundaries.

The real part of the semicircles has to do with the dielectric loss. As observed in Fig. 4, the maximum value of the real part of the semicircles and the dielectric loss (Table 1) increase when the ZrO_2 concentration increases. This means that the polarization becomes an energetically more expensive process when the ZrO_2 concentration is higher. In the conventional case this effect could be due to the distortion in the lattice produced by the core–shell structure and the strain introduced by the solid solution formation. Since the diffusion process is more efficient in the MA case, the core–shell structure could not be formed in such a way that a more relaxed structure is obtained. Therefore, in the MA samples, the loss factor (Table 1) is smaller than those measured in the conventional samples. The lattice distortion could be responsible for the reduction in the K values when the ZrO_2 content increases (Table 1).

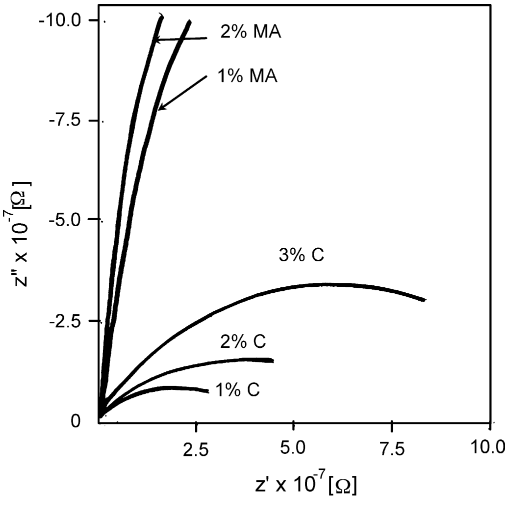

Fig. 4. Impedance complex curves for conventional (C) and mechanically alloyed (MA) samples. The range of the applied frequencies was from 1 Hz to 3.2 MHz.

Table 1
Resistivity, dielectric constant and loss factor of conventional and mechanically alloyed samples

Sample	Resistivity ($\times 10^7$ Ω m)	K	tan δ (1 kHz)
1 wt.% conventional	5.9	576	0.33
2 wt.% conventional	9.0	349	0.356
3 wt.% conventional	18.3	272	0.225
1 wt.% MA	59.7	539	0.035
2 wt.% MA	128.4	203	0.043

The resistivity and dielectric constant were calculated assuming an equivalent circuit composed by a resistance and a capacitor in parallel.

4. Conclusions

1. Abnormal grain growth is presented at lower values of ZrO_2 concentration in MA samples as compared to conventional samples which implies much better diffusion of ZrO_2 in MA samples.
2. Smaller grain sizes can be obtained when mechanical alloying is used.
3. The electrical properties seem to be mainly controlled by the grain boundary characteristics.
4. Mechanically alloyed samples present lower loss factors as compared to the conventional samples.

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