

Properties of bismuth-strontium titanate ceramics doped with MnO₂ and Nd₂O₃

Resumo

Cerâmicas de titanato de bismuto-estrôncio (SBT) dopadas com 4 % em mol de MnO₂ (SBT+Mn) ou Nd₂O₃ (SBT+Nd) foram produzidas através do método convencional de mistura de óxidos. As propriedades estruturais, dielétricas e piezoelétricas foram comparadas entre as cerâmicas puras e dopadas. A razão de aspecto dos grãos (Comprimento/Espessura – C/E) foi modificada com a adição dos dopantes, sendo mais evidente nas cerâmicas SBT+Mn. A adição de neodímio aumentou o fator de acoplamento eletromecânico das cerâmicas enquanto que a dopagem com manganês favoreceu a redução deste parâmetro. Os valores do campo coercitivo, da polarização remanescente e de saturação para as cerâmicas SBT+Mn foram maiores que aqueles obtidos para as cerâmicas SBT e SBT+Nd. **Palavras-chave:** Propriedades dielétricas. Ferroelétrico. Perovskitas. BLSF.

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Abstract

Strontium bismuth titanate samples (SBT) doped with 4-mol % of MnO₂ (SBT + Mn) or Nd₂O₃ (SBT + Nd) were produced by conventional oxide mixture method. The structural, dielectric and piezoelectric properties were compared between the pure and doped ceramics. The aspect ratio of the grains (Width/Thickness – W/T) was modified with the addition of the dopants, being more evident in the SBT + Mn ceramic than in the others. The neodymium addition increased the electromechanical coupling factor of the ceramics while the manganese doping favored the reduction of this parameter. The values of coercive field, saturation and remanent polarization for the SBT + Mn ceramic were higher than that obtained to SBT and SBT + Nd ceramics.

Keywords: Dielectric properties. Ferroelectric. Perovskites. BLSF.

1 Introduction

Bismuth layer-structure ferroelectrics ceramics, abbreviated BLSF, presents plate-like grains which in high orientation has interesting properties, like lower dielectric constant, larger piezoelectric anisotropy, larger spontaneous polarization and lower values of dielectric constant when compared with perovskite-type compounds such as conventional lead zirconate-titanate ceramics (PZT).

Initially strontium-bismuth titanate ceramics (SBT) studied by Subbarao (Subbarao, 1961). He showed that this compound has lower dielectric constant ($\kappa \cong 200$) than a lot of ferroelectrics ceramics, but this value is close to bismuth titanate ceramics ($\kappa \cong 190$) (Gelfuso, 1994). Its structure is composed by bismuth ions linked with oxygen atoms, forming a tetrahedron structure. The bismuth and strontium atoms occupy the A-site and titanium ion in coordination with six oxygen, occupy the B-site, composing the perovskite structure.

The general formula is given by:



where A are mono-, di- or trivalent ions or a mix of them, B could be Ti⁴⁺, Nb⁵⁺, Ta⁵⁺ etc, and m = 3, 4 and 5 which represents the numbers of perovskite layer in the atomic structure.

Such as all BLSF materials, the crystal structure of SBT promotes a plate-like morphology with the Bi₂O₂²⁺ layers parallel to the basal plane of the platelets. The major component of the spontaneous polarization lies in the perovskite plane (Cummins *et al*, 1968). This two-dimensional restriction on the electric dipole rotation would be the reason it is not possible to obtain large coupling factors as those obtained for PZT ceramics.

Newnham and Wolfe (Newnham *et al*, 1969) studied the rare-earth ions effect in bismuth titanate ceramics. They observed that rare-earth ions prefer the Bi³⁺ position in the perovskite layer, near to the tetrahedron layer.

This result was similar for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (Armstrong *et al*, 1972) and $\text{Na}_{0,5}\text{Bi}_{4,5}\text{Ti}_4\text{O}_{15}$ (Newnham *et al*, 1967) ceramics.

Ikegami studied SBT ceramics doped with Cr_2O_3 and MnO_2 (Ikegami *et al*, 1974). Samples doped with Cr_2O_3 have little effect on poling characteristics, but those doped with MnO_2 improve remarkably its dielectric properties. The improvement in poling characteristics means: high values of thickness coupling factor (k_t), planar coupling factor (k_p) and piezoelectric coefficient (d_{31}) obtained for the same poling electric field.

In the present work, 4-mol % Nd_2O_3 or MnO_2 were added in SBT ceramics. The dielectric, piezoelectric properties, changes in microstructure and sintering process were studied in these ceramics.

2 Experimental procedures

Ceramics powders were produced by conventional oxide mixture method. The average particle size determined to raw materials Bi_2O_3 (99,9 %), TiO_2 (98%) and SrCO_3 , were 6,08 μm , 4,87 μm and 1,74 μm , respectively.

The raw materials were mixed in the following stoichiometric proportion:



The oxides were mixed with distilled water in a ball mill, dried in a conventional microwave oven for 30 minutes, and then calcined in an alumina crucible for 24 h at 800 °C. This temperature was determined from differential thermal analysis (DTA) with heating rate of 5 °C/min (Fig. 1).

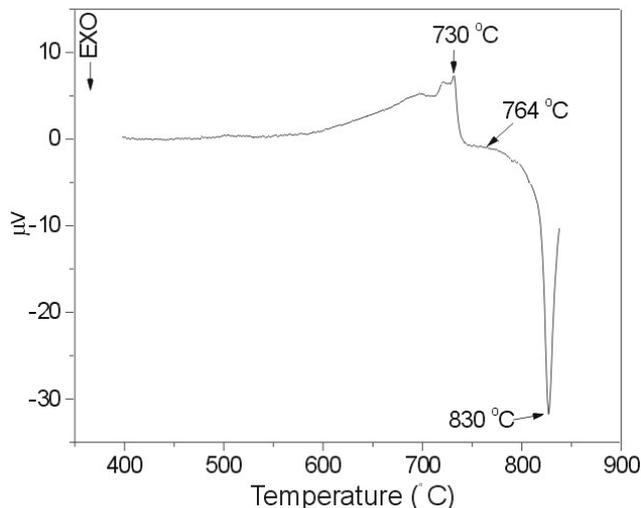


Figure 1: Differential thermal analysis curve of the oxides mixture to produce SBT powder.

It is noticed the presence of a endothermic peak at 730 °C due to the formation of bismuth titanate (Gelfuso, 1994) and a exothermic pick that begins at 764 °C and reaches the maximum at 830 °C, meaning the incorporation of strontium in the structure (Gelfuso *et al*, 1999). Through X rays diffraction (XRD) analysis, the exclusive presence of SBT was confirmed (Fig. 2).

Calcined powders of SBT were mixed with 4-mol% of manganese oxide (SBT+Mn) or neodymium oxide (SBT+Nd), in a ball mill for 1h with distilled water. The mixture was dried to the air in muffle. After that, ten green samples of each composition with density about 4.0 g/cm^3 were conformed in disc shape with 14 mm in diameter and 2 mm in thickness. The discs were sintered at 1160 °C for 3 h in the air and no weight loss was observed after firing. Scanning electron microscopy (SEM) observations were used to verify the grain orientation and to reveal the morphology of the grains. Image analyzer software was used to measure 100 grains in which the width (W) and thickness (T) of the grains were measured to calculate the aspect ratio (W/T).

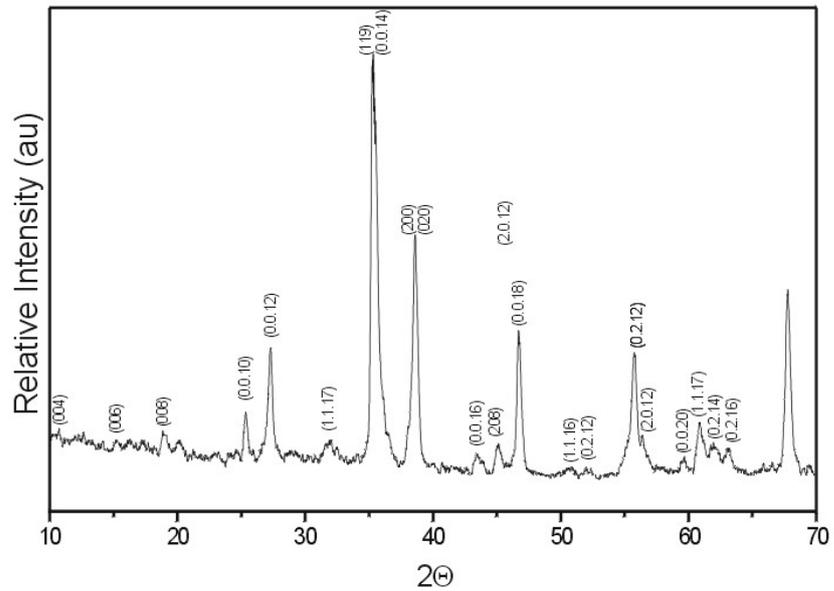


Figure 2: XRD curve of SBT powder calcined at 800 °C to 24 h.

The parallel surfaces of the samples were polished with powder of silicon carbide 800 mesh to reach 0.5 mm in thickness. Dielectric and piezoelectric characterizations were done as a function of poling time and electric field strength. Hysteresis loops were observed at 60 Hz using a Sawyer-Tower circuit, with the samples immersed in silicon oil at 120 °C. The samples were poled at dc electric field of 10 kV/mm in silicon oil at 120 °C for 1 h.

3 Results and discussions

Table 1 presents the densities (ρ) of the sintered samples, the average values of W and W/T obtained for SBT, SBT+Mn and SBT+Nd ceramics. An increase of densification in SBT+Mn could be observed and an inverse effect was noted for SBT+Nd when compared with the SBT samples. Ikegami (Ikegami *et al*, 1974) also observed the effect of increased densification in MnO₂ doping bismuth titanate.

Table 1: Medium width (W), aspect ratio (W/T) of the grains and density of the SBT, SBT+Mn and SBT+Nd samples.

	SBT	SBT+Mn	SBT+Nd
W (μm)	23,3 \pm 2,6	5,7 \pm 0,4	7,2 \pm 0,9
W/T	12,0 \pm 1,1	5,1 \pm 0,5	16,1 \pm 1,2
ρ (g/cm ³)	6,9 \pm 0,2	7,2 \pm 0,3	6,5 \pm 0,2

In addition, it can be noted the reduction of approximately four times the average grain size of SBT+Mn and three times for SBT+Nd when compared with SBT samples, besides the smallest dispersion for the sample doped with manganese. The W/T value was altered to the ceramics containing dopants, being more evident in that doped with MnO₂, turning it more "spherical" than the other ones, which increased the curvature size of the grains favoring the sintering process. The inverse effect was observed in SBT+Nd, causing the smallest density between the ceramics.

Figure 3 exhibits the surfaces of the samples A) SBT, B) SBT+Mn and C) SBT+Nd. It can be noted that the ceramic doped with manganese ions, presents a microstructure of grains with a very-defined plate-like format and a narrow granulometric distribution. The morphology of the grains for the sample doped with neodymium oxide also come in the form of plates but it is observed the exaggerated growth from some of them.

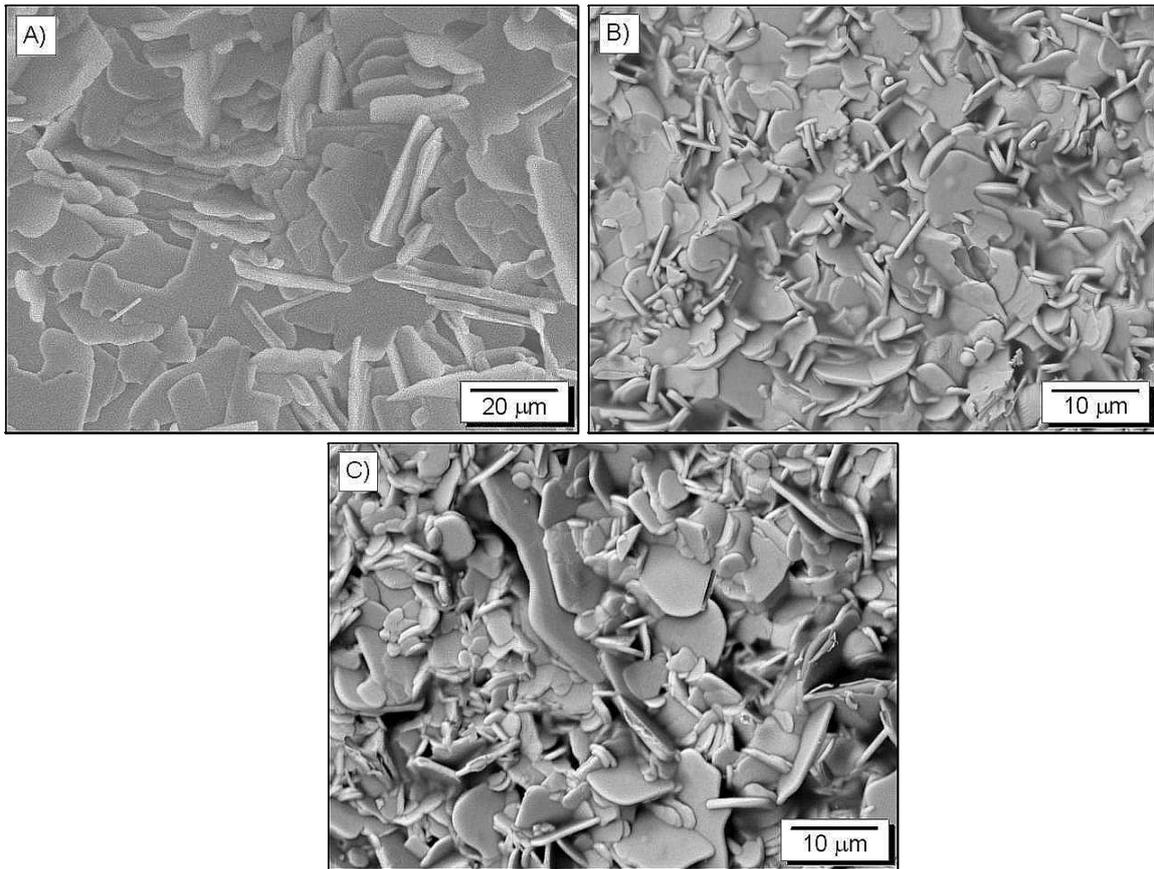


Figure 3: Surfaces of A) SBT, B) SBT+Mn and C) SBT+Nd ceramics.

Figure 4 shows the behavior of the dielectric constant (k) of the SBT and those doped vs. poling time. Comparing the k values of pure SBT and the doped ones, it is observed an increase for SBT+Nd and the reduction for SBT+Mn. Studies accomplished by Wu (Wu et al, 1983) based on perovskite lead (PZT) doped with Mn ceramics showed the same tendency. He classified this element as stabilizer of properties because its anomalous behavior in relation to the well-known elements as acceptor (Fe^{3+} , Ni^{2+}). Wu observed the increasing effect of the dielectric constant for small poling electric field, in this way he noticed the reduction of the dielectric constant. This effect was explained by Uchida (Uchida, 1965) as being caused by the rotation of the domains of 90° . The rotation of these domains is more effective than the ones of 180° , beside that the applied electric field increases. The return of the 90° domains is slow with the addition of Mn ions and probably that is the cause of the smallest values of k for the SBT+Mn samples.

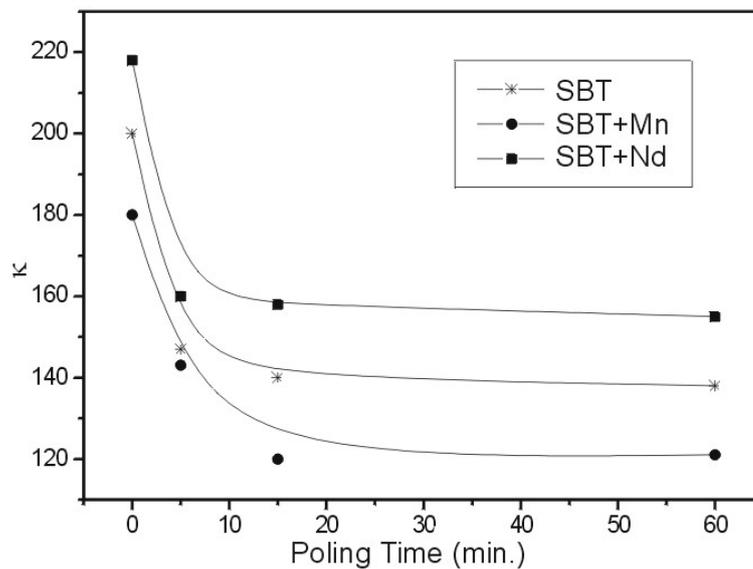


Figure 4: Dielectric constant of the SBT samples and SBT doped vs. poling time.

In the Figure 5, the reduction of the k_t values is presented for SBT+Nd samples and this property increases in an accentuated mode for SBT+Mn when compared with the pure ceramic of SBT. Besides that, it can be seen that k_t practically saturates with poling time of 30 minutes, which is not verified for SBT. The k_t values for the SBT+Mn samples were higher to those found in literature ($k_t = 22\%$) (Ikegami *et al*, 1974) that tells behavior of doped samples with 5-mol % of manganese. The high values for the electromechanical coupling factor of these samples can be a consequence of the formation of vacancies, explained by Wu (Wu *et al*, 1985) and the distortion of the crystal caused by the Mn ion addition in the B-site (Newham *et al*, 1971).

Figure 6 shows the hysteresis loops for the pure and doped SBT ceramics. It can be observed the higher coercive field, saturation and polarization for the ceramic doped with manganese with the others ceramics. As shown previously, Uchida (Uchida, 1965) observed that the rotation of the 90° domains is more effective than the 180° domains and with the addition of manganese ions, the return of 90° domains are slow, in this way coercive field, remnant and saturation polarization were larger to these ceramics.

Warren (WARREN *et al*, 1995) reported that oxygen vacancy in this ferroelectric compounds plays detrimental roles in the fatigue properties, it can stabilize the charges trapped at domain wall, and make the unpinning of domain wall difficult. Recent studies (SIMÕES *et al*, 2006) have shown that Sr–Ti–O blocks are very stable, they lead to a less concentration of oxygen vacancy in SBT compounds and thus prompt the unpinning rate of domain wall.

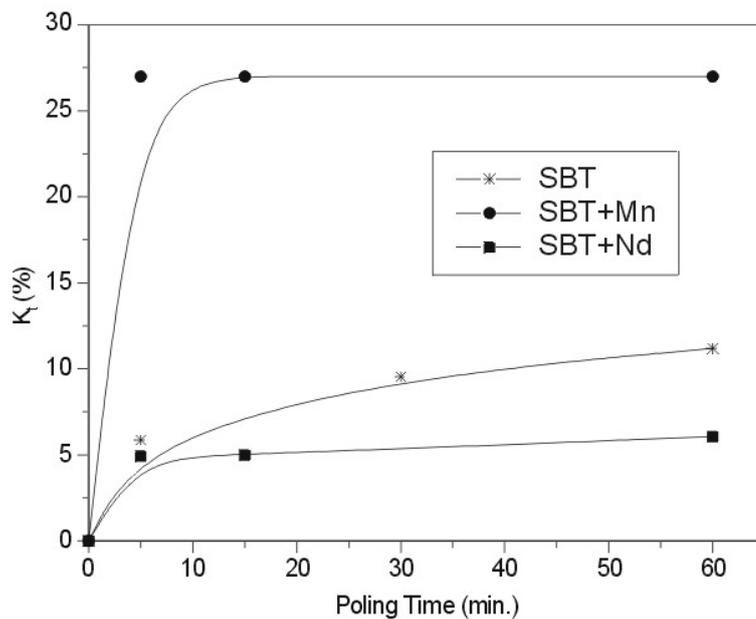


Figure 5: Electromechanical coupling factor k_t vs. poling time for pure and doped SBT ceramics.

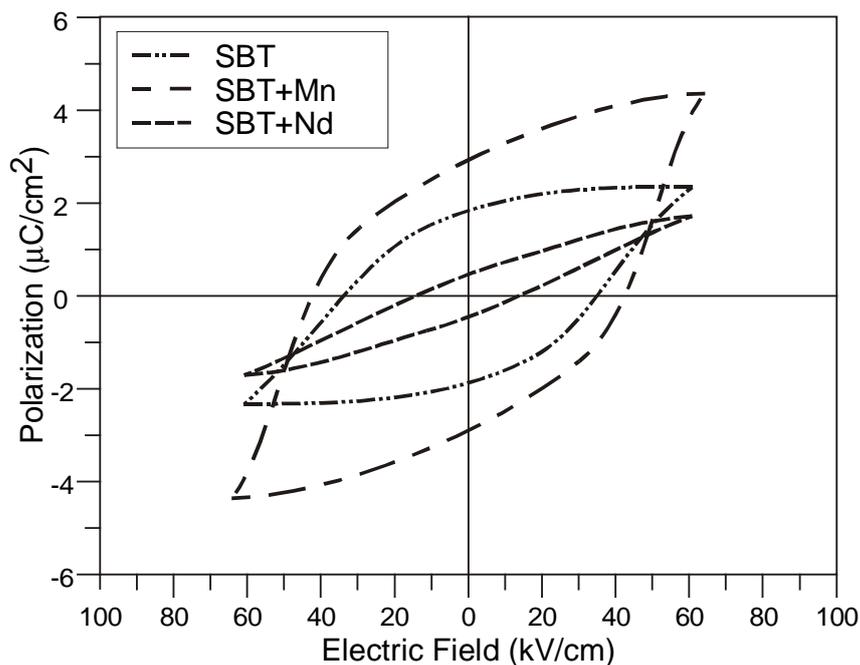


Figure 6: Hysteresis loops to SBT, SBT+Mn and SBT+Nd samples.

4 Conclusions

In the SBT ceramics doped with MnO_2 and Nd_2O_3 , the influence was observed in the dielectric, ferroelectric and piezoelectric properties and in the densification caused by morphologic changing of the grains (aspect ratio).

The grains of SBT+Mn ceramics have shown a more spherical shape, presenting a low aspect ratio, increasing the curvature ratio of the grains favoring the sintering process. The SBT+Nd samples present an exaggerated growth of some grains and the high aspect ratio decreases the densification of these ceramics.

Comparing the k values of pure and doped SBT ceramics, it was observed an increase for SBT+Nd and the reduction for SBT+Mn, probably caused by the slow rotation of 90° domains with the addition of Mn ions. The higher k_r , saturation and remnant polarization values suggest that this effect is present.

The ceramics doped with manganese obtained higher values of electromechanical coupling factor than those reported in literature and dielectric constant values were smaller than the other ones because of the mobility of the 90° domains.

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