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# Hydrothermal synthesis of perovskite based materials for microelectronic applications

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The hydrothermal technique was used as a perspective method to synthesize barium strontium titanate (BST) bulk materials with nanocrystalline structure. X-ray diffraction, SEM/EDS and dielectric measurements were performed on BST sintered pellets. The results thus obtained are of interest for the optimization of the manufacturing process of perovskite bulk ceramics by controlling synthesis parameters (concentration, temperature, time) and sintering temperature.

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*Keywords*: Powders-hydrothermal synthesis, Nanostructured materials, Dielectric properties

## 1. Introduction

Perovskite based materials are widely studied for technical microelectronic applications [1-5]. Lead containing perovskites such as $PbZr_xTi_{1-x}O_3$ are by far the best performing for actuators, transducers, and a range of sensors [6]. In recent years considerable effort has been made in the controlled synthesis of crystalline materials and thin films of barium strontium titanate which typically exhibit nonlinear optical coefficients and large dielectric constants.

Understanding the behaviour of ferroelectric materials at the nanoscale dimension is of importance to the development of molecular electronics. Metal oxides with a perovskite structure present dielectric, piezoelectric, electrostrictive, pyroelectric and electro-optic advantageous properties for applications in the electronic industry, such as: imaging devices, optical memories, modulators, deflectors, transducers, actuators, high-k dielectric constant materials [1-6]. These properties are strongly dependent on the metallic elemental ratios, impurities, microstructure and grain sizes. In the literature [7] several routes to synthesise nanostructured materials are described, namely: wet chemical, mechanical, form-in-place and gas phase synthesis. Hydrothermal technique is one of the wet chemical synthesis routes with a high potential to lead to nanoparticles. Hydrothermal synthesis is a soft solution processing (SSP) [8] which allows in situ fabrication of shaped, sized, oriented ceramic materials without firing, sintering or melting steps. The advantages of the hydrothermal technique are [9]: the duration of the experiments is reduced by two orders of magnitude compared to classical synthesis procedures; crystal size, morphology and the level of agglomeration for different ceramic oxides can be controlled as a function of the hydrothermal synthesis parameters; it is an environmentally friendly procedure; the costs for the instrumentation, energy and precursors are lower comparing to other synthesis routes.

Various compositions of barium strontium titanate (BST) perovskite ceramics are studied for their electrical properties for a wide range of applications.

In [10] it was shown that BST materials doped by MgO and $Mn_2O_3$ offer an attractive solution for tunable microwave devices.

$Ba_xSr_{1-x}TiO_3$ compositions with $x>0.7$ are ferroelectric at room temperature. The transition temperature ($T_C$) of $Ba_xSr_{1-x}TiO_3$ decreases with the increase of Sr concentration and varies between 393 K for pure $BaTiO_3$ and <50 K for high $SrTiO_3$ content compositions ($SrTiO_3$ is an incipient ferroelectric and its dielectric permittivity increases with the decrease of the temperature, reaching a maximum near 0 K and no ferroelectric transition is observed) [11].

In the present work, based on this data, we have used hydrothermal method to synthesize $Ba_{1-x}Sr_xTiO_3$ (x in the range 0.2-0.25) bulk materials.

Nanocrystalline BST based materials were obtained and their dielectric properties were measured and compared to the literature data for (sub) micrometric samples.

## 2. Experimental

Ba (II), Ti(IV), Sr(II) aqueous solutions were used as starting materials for barium strontium titanate synthesis. These solutions were mixed with an appropriate amount of mineralise reagent (KOH). Powders based on $Ba_{1-x}Sr_xTiO_3$ were then precipitated in Teflon autoclaves (temperature in the range 150-200 $^oC$, pressure 4.5 bar, time 3 hours, at very alkaline pH values). The hydrothermal treatment time was selected according to previous studies [12]. Powders thus obtained were bounded with polyvinyl alcohol, granulated and pressed at 800-1000 MPa. Green pellets (11 mm in diameter and 1.5 mm thick) were sintered

2 hours, at 1200-1250 °C and a heating rate of 5 °C/min, in a CARBOLITE RHF 17/3 furnace. Density of green and sintered pellets was measured using the standard Archimedes method. Chemical quantitative analysis (inductively coupled plasma - ICP, direct coupled plasma – DCP, atomic absorption spectroscopy –AAS) and microstructures investigations (XRD using X-ray diffractometer Rigoku/CuKα radiation Geigerflex C/max-C series; SEM/EDS using HITACHI S 4100 Scanning Electron Microscope) were performed to characterise BST powders and sintered products. The sintered pellets were lapped to make the surfaces flat and parallel. Colloidal gold was applied to both flat surfaces to get metal electrodes. Dielectric constant and losses have been measured in the temperatures range of 30-140 °C at frequencies in the range 100 Hz - 1MHz, using an apparatus HP 4284A Precision LCR Meter. Some of the synthesised samples are presented synthetically in Table 1.

*Table 1. Hydrothermal synthesised samples.*

| No. | Sample type | Sample name | | Synthesis parameters | Sintering parameters |
|---|---|---|---|---|---|
| 1 | BST | B1 | P26 | 150 °C/3h | 1250 °C/2h |
| 2 | | | P27 | 150 °C/3h | 1250 °C/2h |
| 3 | | B2 | P22 | 200 °C/3h | 1250 °C/2h |
| 4 | | | P23 | 200 °C/3h | 1250 °C/2h |
| 5 | | | P24 | 200 °C/3h | 1250 °C/2h |
| 6 | | | P25 | 200 °C/3h | 1250 °C/2h |

## 3. Results

Fig. 2 shows the X-ray diffraction patterns for BST sintered pellets prepared by the hydrothermal method.

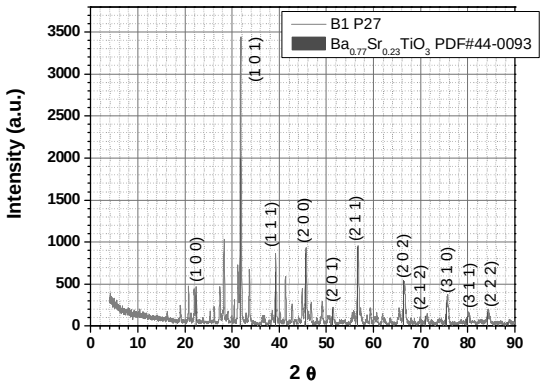



*Fig. 2a. B1 P27 (sintered at 1250 °C/2h).*

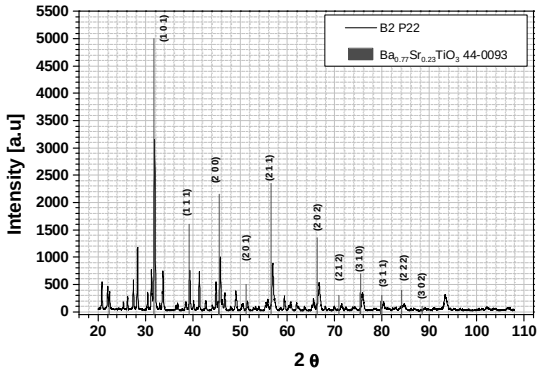


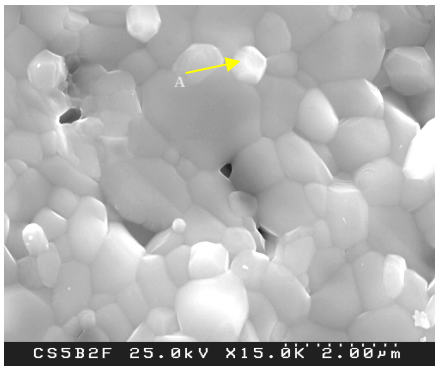

*Fig. 2b. B2 P22 (sintered at 1250 °C/2h).*

*Fig. 2. X-ray diffraction patterns for BST sintered pellets synthesised in hydrothermal conditions.*

Figs. 3 and 4 show the scanning electron micrographs of BST (B1P26 and B2 P23 samples) sintered at 1250 °C/2h and thermally etched at 1200 °C/4min.

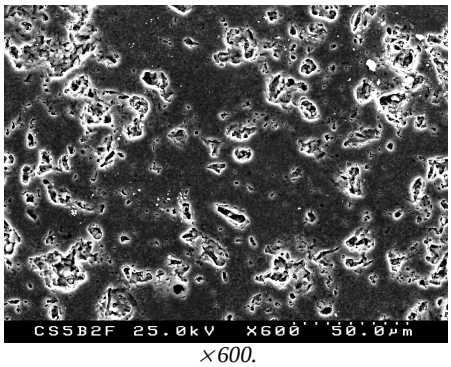
Figs. 5 and 6 show the permittivity and dielectric loss tangent dependence upon temperature at various frequencies in the temperature range 30°-140 °C.

a



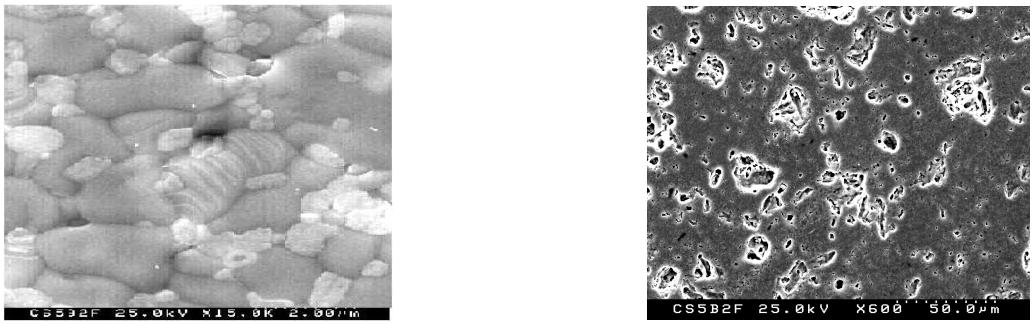

×15000.

b




×600.

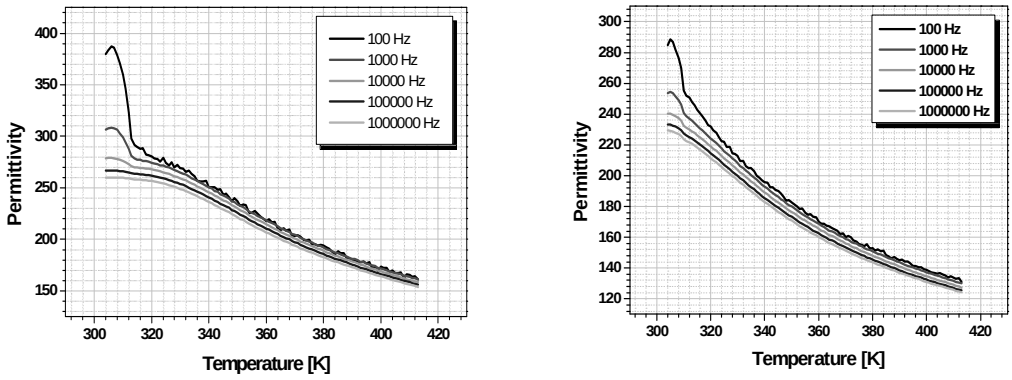
*Fig. 3. SEM micrographs of BST (B1 P26, 150 °C/3h, sintered at 1250 °C/2h).*




×15000.
a

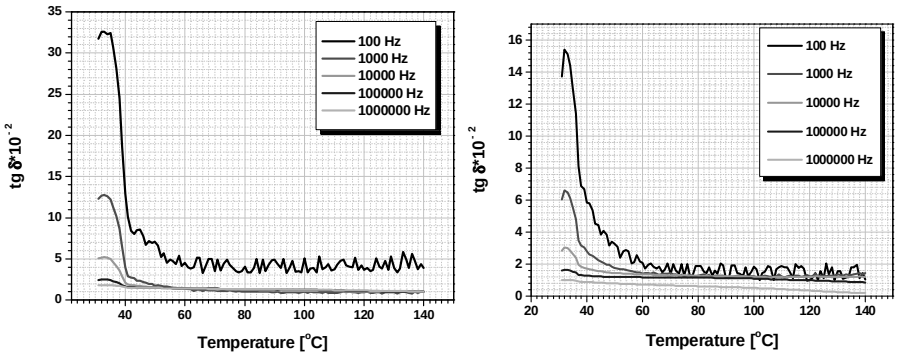
×600.
b

*Fig. 4. SEM micrographs of BST (B2 P23, 200 °C/3h, sintered at 1250 °C/2h).Cross section images.*




a b

*Fig. 5. Permittivity as a function of temperature for BST bulk ceramics sintered at 1250 °C/2h.*
*a. B1 P26 sample (150 °C/3h); b. B2 P23 sample (200 °C/3h).*




a b

*Fig. 6. Dielectric loss tangent of B1 P26 and B2 P23 samples.*
*a. B1 P26 sample (150 °C/3h); 6b. B2 P23 sample (200 °C/3h).*

## 4. Discussions

The X-ray diffraction patterns from Fig. 2 reveal a polycrystalline material with characteristic peaks of $Ba_{0.77}Sr_{0.23}TiO_3$ (according to JCPDS 44-0093) as main phase. Other phases containing barium are identified, namely: $Ba_{1.91}Sr_{0.09}TiO_4$ (according to JCPDS 13-0522) and $Ba_{0.6}Sr_{0.4}TiO_3$ (according to JCPDS 34-0411).

Figs. 3 and 4 relieve that the residual porosity is higher for sample B1 than for sample B2 and a bimodal distribution of the grains in both samples with nano to submicron size of about 200-600 nm can be observed. HRTEM analysis for B1 P26 and B2 P23 powder precursor also indicated small crystallites size of about 5-10 nm [13]. Energy dispersive X-ray spectroscopy (EDS) indicates that the main elements of BST (Ba, Sr, Ti) are present but strontium has a non-uniform distribution, higher in the case of sample B1. This is in accordance with predicted thermodynamic parameters of hydrothermal synthesis of BST using specialized software and confirms XRD results were it could be seen that one main phase is present ($Ba_{0.77}Sr_{0.23}TiO_3$) and probably $Ba_{1.91}Sr_{0.09}TiO_4$ and $Ba_{0.6}Sr_{0.4}TiO_3$ as secondary ones.

Dielectric measurements (Fig. 5) relieve for BST ceramics a phase transition near room temperature (~33-34 $^oC$) independent of the hydrothermal synthesis conditions, which is a typical $T_C$ value for $Ba_xSr_{1-x}TiO_3$ compositions with x>0.7. Both BST samples (B1 and B2) are in the ferroelectric state at room temperature. The obtained permittivity values are lower for the samples

B 1 and B 2 independent of the hydrothermal conditions comparing to the literature data for micro grained sized materials ($\varepsilon$ in the range 4000 - 10000). A reasonable explanation could be: the initial powders are nanocrystalline and they are very difficult to be consolidated due to their low apparent density, low flow rate, high adsorbed gases, high surface area and large friction between particles. It is expected that the final theoretical densities for fully consolidated nanomaterials to be lower than for micro grained sized materials due to a large contribution of lower grain boundaries [14]. The heterogeneity of the phases in the sintered materials could be also a possible explanation of the obtained dielectric permittivity values.

As expected the dielectric permittivity decreases with the increase of the frequency, for both samples. Values of the dielectric constant for the hydrothermal sample synthesized at 150 $^oC$ are in the range 150-400. Despite the higher porosity of the B1 ceramic samples than B2 samples, B2 samples have lower dielectric constant values (120-300). The variation of dielectric losses versus temperature depicted in Fig. 6 shows a lower tg$\delta$ for B2 (synthesised in hydrothermal conditions at 200 $^oC$/3h) than for B1 sample (synthesised in hydrothermal conditions 150 $^oC$/3h).

Lower dielectric permittivity and dielectric loss tangent values obtained for sample B2 could be explained by its lower crystallite sizes, knowing from the literature that some of the electric characteristics values decrease with decreasing crystallite sizes [6]. Based on these preliminary characterizations, the manufacturing process of BST powders and BST bulk ceramics will be optimized controlling synthesis parameters (concentration, pressure, temperature, time).

## 5. Conclusions

Nanocrystalline BST based perovskite materials were obtained in hydrothermal conditions. The dielectric characteristics were measured. The sizes of the crystallites have an important influence on the powder processing and the electrical characteristics of the sintered pellets. The exact role played by the dopants on the dielectric properties of barium titanate is not precisely known, especially at high frequencies where the electronic polarisation mechanism which accounts for 2/3 of the total polarisation, remains the only active one.

Additional work is needed to establish which factors (grain size or doping atoms) are dominant.

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