COMPOSITION CONTROL OF FERROELECTRIC NANOPARTICLES USING SUPERCRITICAL FLUIDS

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Pure and well-crystallized Barium Strontium Titanate (BST) nanoparticles with controlled Ba/Sr ratio have been successfully synthesized under supercritical conditions using a continuous-flow reactor in the temperature range of 150-380°C at 26 MPa. To synthesize the $Ba_{0.6}Sr_{0.4}TiO_3$ composition, alkoxides, ethanol and water were used. The resulting nanopowder consists of fine particles with an average particle size of 23 nm. The results show that the Ba/Sr ratio of this powder can be accurately controlled from the composition of precursor. The characterization of the as-synthesized $Ba_{0.6}Sr_{0.4}TiO_3$ solid-solution and the dielectric properties of the sintered ceramics are here reported.

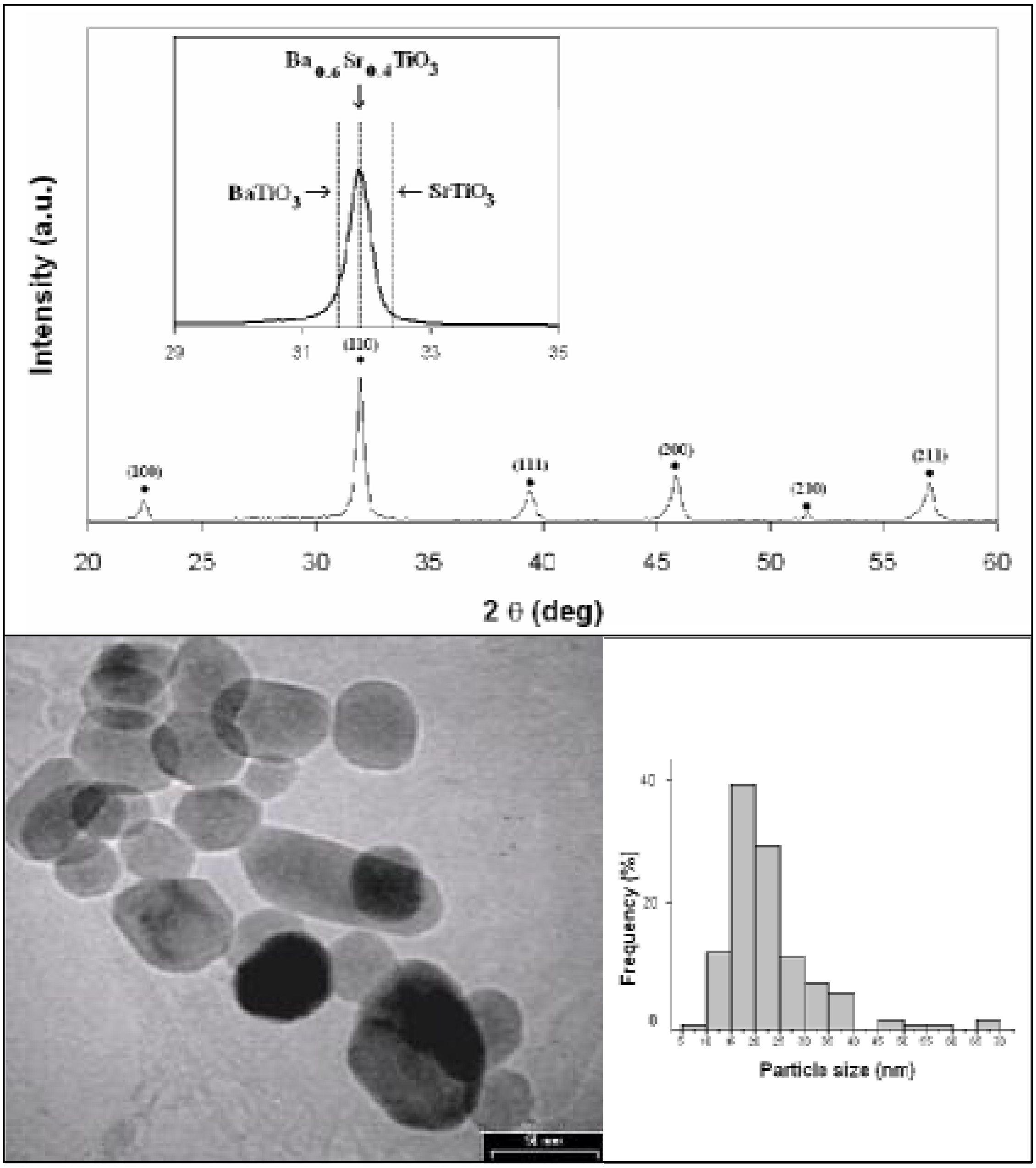
INTRODUCTION

The current miniaturization in microelectronics and telecommunications is driving the size of raw materials to the nanoscale. Barium titanate ($BaTiO_3$) belongs to the family of the perovskite-type structure and is an important material in electronic industry, due to its high dielectric constant (permittivity) and its good ferroelectric properties [1]. Furthermore, the increase in permittivity observed on fine-grained $BaTiO_3$ ceramics (<1 μm) has motivated the interest for new synthesis routes for nanoparticles. The use of these nanoparticles not only allows the enhancement of the ferroelectric properties or device miniaturization but also a decrease of the sintering temperature and thus of the overall production cost. As reported elsewhere, thanks to supercritical fluids properties[2], ultrafine pure and well-crystallized $BaTiO_3$ nanoparticles can be successfully obtained in a one-step process, without the long and tedious steps of post-treatments, associated with other synthesis methods (sol-gel, precipitation, solid state reaction)[3]. Single-crystalline $BaTiO_3$ shows an impressive dielectric constant peak value at the ferroelectric to paraelectric phase transitional Curie temperature (T_c) close to 122 °C[4]. The substitution of Ba by Sr allows decreasing linearly this temperature and the ferroelectric phase transition in $Ba_{0.6}Sr_{0.4}TiO_3$ occurs near room temperature. It was then an interesting challenge to adapt the supercritical fluid $BaTiO_3$ synthesis process to the synthesis of the barium strontium titanate $Ba_{0.6}Sr_{0.4}TiO_3$. The key points of the present report are: (i) well-crystallized barium strontium titanate (BST) nanoparticles can be prepared under supercritical conditions using a continuous-flow reactor without carbonate pollution, (ii) tedious steps such as drying, washing and calcining are not necessary and (iii) the composition of BST solid-solution can be easily controlled by setting the initial Ba/Sr composition of precursor.

I – SYNTHESIS OF $Ba_{0.6}Sr_{0.4}TiO_3$ NANOPARTICLES

Nanopowders of $Ba_{0.6}Sr_{0.4}TiO_3$ were produced under supercritical conditions using a continuous-flow system through the hydrolysis of a precursor made of Ba, Sr and Ti alkoxides in ethanol. The experimental set-up is described in detail elsewhere [4].

After synthesis, elementary analysis of products was performed by inductively coupled plasma-atomic emission spectrometry (ICP-AES at the CNRS Central Service of Analysis, Vernaison, France). Philips X-ray diffractometer (PW 1820) was used to probe the crystalline state of the as-synthesized powder. The average particle size and morphology were characterized by transmission electron microscopy (TEM JEOL 2000FX). Dry powders were also analyzed by infra-red spectroscopy (FTIR) using KBr pressed pellets.



The pattern of Figure 1 (c) shows that the BST powders are single phased and well-crystallized. All the diffraction lines are in agreement with the lattice parameters of $Ba_{0.6}Sr_{0.4}TiO_3$ which confirms the stoichiometry. Moreover, none carbonate pollution nor parasitic phases were detected.

As shown in Figure (a), the BST ($Ba_{0.6}Sr_{0.4}TiO_3$) powder consists of fine irregular-shaped particles with an average particle size of 23 nm (calculated from several TEM micrographs, JEOL 2000FX). The average particle size of ~21 nm deduced from the (110) XRD peak broadening (Scherrer equation) is fully consistent with the statistical particle size obtained from TEM, suggesting that the nanoparticles are monocrystalline.

II – DIELECTRIC PROPERTIES

In order to probe the dielectric properties of the as-synthesized BST nanoparticles, the powder was uniaxially-pressed into discs (6mm in diameter and 1 mm in thickness). Thanks to thermogravimetric and dilatometric analysis, the optimal sintering conditions of the as-synthesised $Ba_{0.6}Sr_{0.4}TiO_3$ were determined. The temperature cycle applied to the sample was a heating under oxygen atmosphere at a rate of 100 °C min^{-1} up to 1250 °C or 1350 °C and then a dwell of 4 hours.

Sintering at 1250°C leads to low relative density ceramic (65%) displaying a heterogeneous microstructure whereas improved density of 90% is obtained when pellet is sintered at 1350°C.

Dielectric measurements were performed on discs using a Wayne–Kerr component analyser 6425 in the temperature range 50–450 K and in the frequency range 1 Hz–1000 kHz. Gold electrodes were previously sputtered on the circular faces. The real part of the permittivity derived from the capacitance and dielectric losses tan δ (tan $\delta = \varepsilon''/\varepsilon'_r$) were directly measured.

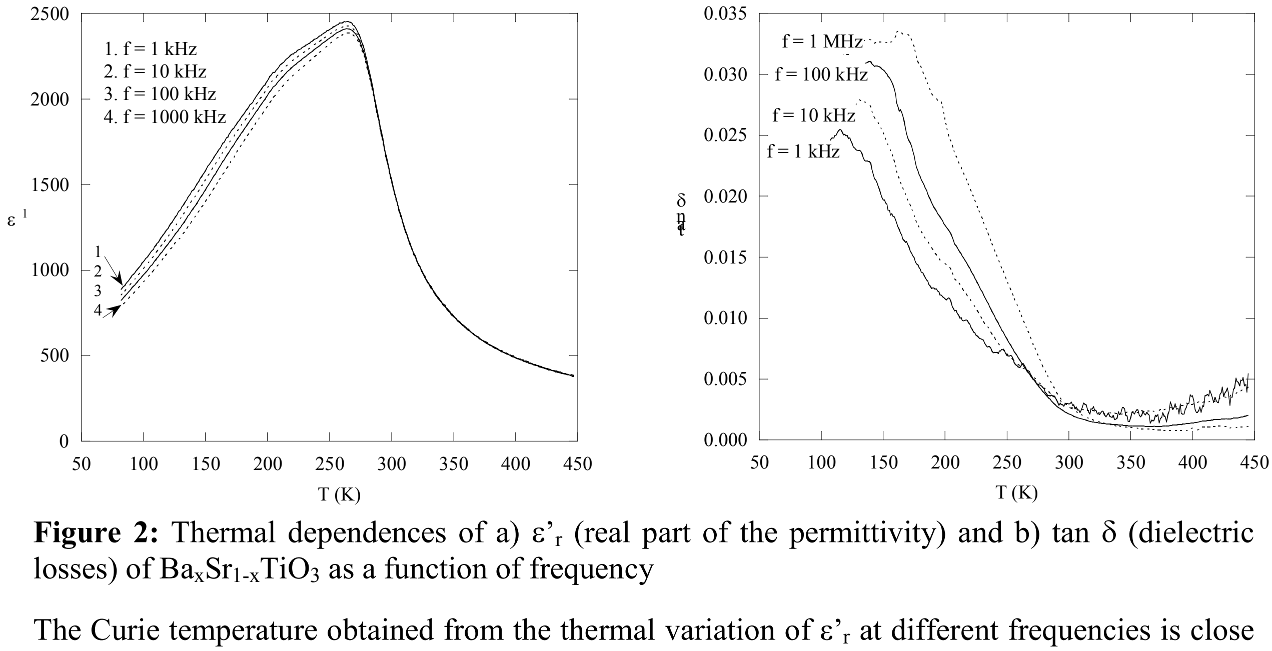


Figure 2: Thermal dependences of a) ε'_r (real part of the permittivity) and b) tan δ (dielectric losses) of $Ba_xSr_{1-x}TiO_3$ as a function of frequency

The Curie temperature obtained from the thermal variation of ε'_r at different frequencies is close to 265K. According to other studies already reported (BST synthesised by solid state reactions or sol-gel), the Tc value of $Ba_{0.6}Sr_{0.4}TiO_3$ varies from 260 to 280K in the litterature. The phase transition is diffuse and the value of the maximum of permittivity is about 2500. Moreover, the permittivity follows the Curie-Weiss law.

The relatively low value of the dielectric permittivity and the smoothness of the transition are thought to be related to the microstructural characteristics. The x-ray diffraction pattern of the as-sintered ceramic fits well with a pure $Ba_{0.6}Sr_{0.4}TiO_3$ but porosity and grain size effect are determinant factors on the dielectric performances.[13] The dielectric losses ($\tan \delta = \varepsilon''_r/\varepsilon'_r$) in the temperature range 250-450K are less than 0.01 (1%) and nearly stable even at a frequency as high as 1MHz. Such values remain in an interesting range for microelectronic applications.

CONCLUSIONS

Using Supercritical Fluids, we are able to synthesize in the form of nanoparticles an important ferroelectric material in the electronic industry: $Ba_{0.6}Sr_{0.4}TiO_3$. The composition can be easily controlled by setting the initial Ba/Sr composition of precursor used in our supercritical fluid process developed by us for $BaTiO_3$ synthesis. The as-synthesized nanoparticles of $Ba_{0.6}Sr_{0.4}TiO_3$ are ultra pure and well-crystallized. In addition to this BST composition, we can successfully synthesize other BST solid-solutions by changing the ratio Ba/Sr in the precursor composition.

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