Synthesis and electric properties of nanoporous $BaTiO_3$

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Ferroelectrics are a very important class of functional materials, particularly in the area of electronics and microelectronics industry. They are used in bulk and film forms and find applications in a huge range of devices from multilayer capacitors, piezoelectric generators, motors, actuators, positive temperature coefficient sensors, integrated optics and memories.[1] Controlling the morphology of ferroelectrics in the nano-scale inputs new energy into the research and development of ferroelectric materials. For example, various 1-dimensional nano-rods, nano-wires and nano-tubes as well as self-assembly of 0-dimensional nano-islands of ferroelectrics have been achieved, providing candidates for both fundamental studies and novel applications of ferroelectricity in nano-scale.[2]

A common thought is that porosity is adverse to both ferroelectric and dielectric materials. Perfect single crystals or dense ceramics are desired in most cases. But actually, porosity may also have good impacts on materials properties of ferroelectrics. A typical example could be porous pyroelectric films which exhibit higher figure of merits over their dense counterparts.[3] Porous piezoelectric ceramics are known to have higher hydrostatic figure of merit and better acoustic impedance matching with ambient medium in applications of low frequency hydrophones and sensors. These effects come from the lowering of dielectric constant of materials due to the introduction of porosity. By manipulating the volume ratio of porosity, dielectric constant can be adjusted in a wide range. Taking advantage of it, materials with highly anisotropic dielectric constant were fabricated with the introduction of aligned pores.[4] In the above cases, pores are usually formed by incomplete sintering or using sacrificial pore formers and exist in between the grains. The negative influence of porosity in these applications is known as the decrease of mechanical stiffness of the materials. If pores reside inside the grains, this would not be a problem any more.

In this work, the synthesis of nanoporous barium titanate prepared by template assisted methodology using cationic cetyltrimethylammonium chloride surfactant[5] or non-ionic block copolymer Pluronic PE 10300 ($EO_{15}PO_{70}EO_{15}$) is reported. The materials were characterized by powder X-ray diffraction, scanning and transmission electron microscopy, low temperature nitrogen adsortion-desorption isotherms and Raman spectroscopy. Well crystallized nanoporous $BaTiO_3$ crystallites were directly synthesized from solution via a simple sol-precipitation process with both types of templates. The nanoporous structures were disordered and wormhole-like with thick single-crystalline framework (Figure 1). The ferroelectric properties of the materials were evaluated by measuring the variation of the dielectric permittivity with the temperature (Figure 2). Using Landauer-Bruggeman effective medium aproximation (EMA) and Spherical Inclusion model (SI), the effective dielectric constants of BaTiO3 porous materials were estimated to be around 2500 for 10 kHz which are similar to those of nano-grain $BaTiO_3$ ceramics (Figure 2).

References:

[1] P. M. Vilarinho, Functional materials: properties, processing and applications, in Scanning Probe Microscopy: Characterization, Nanofabrication and Device Application of

Functional Materials, pag 3 – 33, NATO Science Series, II. Mathematics, Physics and Chemistry – Vol. 186, Kluwer Academic Publishers, 2005.

[2] F. D. Morrison, Y. Luo, I. Szafraniak, V. Nagarajan, R. B. Wehrspohn, M. Steinhart, J. H. Wendorff, N. D. Zakharov, E. D. Mishina, K. A. Vorotilov, A. S. Sigov, S. Nakabayashi, M. Alexe, R. Ramesh, J. F. Scott, *Rev. Adv. Mater. Sci.* **4** (2003) 114.

[3] G. Suyal, A. Seifert, N. Setter, Appl. Phys. Lett. **89** (2002) 1059.

[4] Z.N. Wing, B. Wang,J. W. Halloran et al. J. Am. Ceram. Soc. **89** (2006) 3696.

[5] R.Z. Hou, P. Ferreira, P. M. Vilarinho, Micropor. Mesopor. Mater. (2007) doi:10.1016/j.micromeso.2007.06.051

Figures:

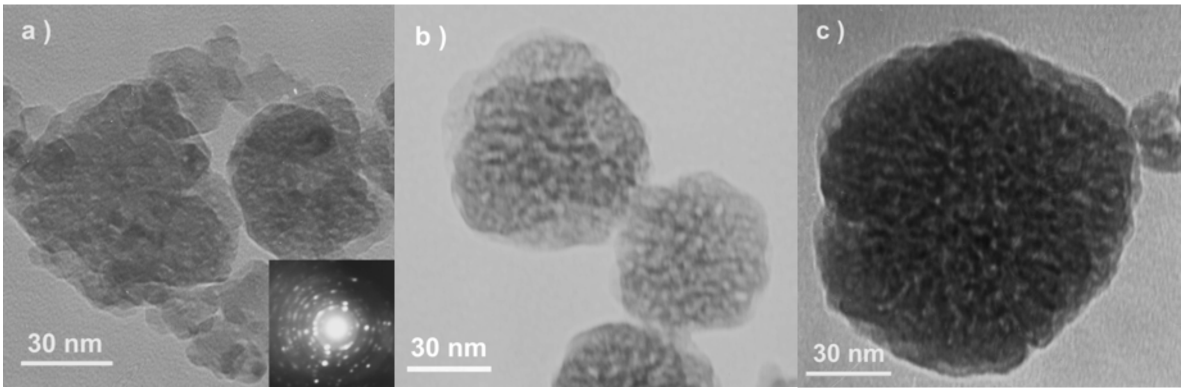

Figure 1. TEM images of nanoporous $BaTiO_3$ prepared with PE 10300: a) as-synthesized crystallites (selected area electron diffraction is shown as inset); b) calcined at 573 K and c) calcined at 673 K.

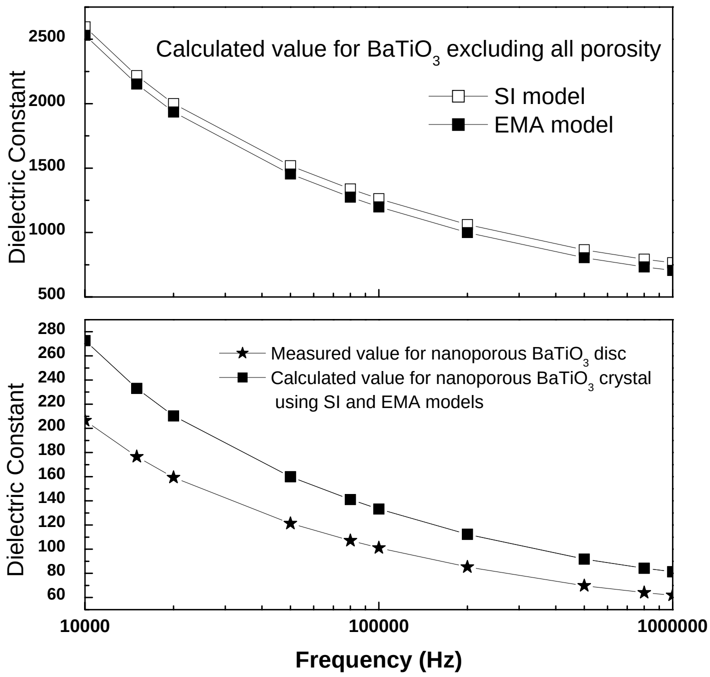

Figure 2. Dielectric characterization on isostatic pressed discs composed of nanoporous $BaTiO_3$, based on which, the apparent dielectric constants of nanoporous $BaTiO_3$ crystallites and $BaTiO_3$ without any porosity are estimated using both SI and EMA models. For nanoporous $BaTiO_3$ crystallites, using SI and EMA results in very close values.