J Mater Sci (2006) 41:5743–5745
DOI 10.1007/s10853-006-0103-y

LETTER

# Preparation and characterization of nanosized barium calcium titanate crystallites by low temperature direct synthesis

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Received: 14 April 2005 / Accepted: 23 September 2005 / Published online: 13 May 2006

Over the past decade, the effect of impurities on characteristic of $BaTiO_3$ has been widely studied. Calcium is one of the most common impurities doped in the $BaTiO_3$ ceramics. It has been reported [1–3] that $Ca^{2+}$ can occupies $Ba^{2+}$ as well as $Ti^{4+}$ sites. There are no direct evidences given into the $Ca^{2+}$ cation substitution. Hence the formula $BC_xT$, where x represents the initial molar ratio of $[Ca^{2+}]/[Ba^{2+} + Ca^{2+}]$, is adopted in this paper so as to imply no a priori commitment of the place occupancy of $Ca^{2+}$ ions in $BaTiO_3$ lattices. The partial replacement of $Ba^{2+}$ by $Ca^{2+}$ was reported [3–5] to broaden the temperature dependence of the dielectric constant, improve the electromechanical behavior, and inhibit the formation of the unwanted hexagonal phase of $BaTiO_3$. While the $BaTiO_3$ ceramics with $Ca^{2+}$ occupying $Ti^{4+}$ sites can be co-sintered with Ni electrodes under a reducing atmosphere without changing into semiconductor.

In view of the commercial importance, calcium substituted $BaTiO_3$ now has been reinvestigated with specific emphasis on the synthesis routes. Conventional BCT powders were prepared [3, 6–9] by solid-state reaction between a mixture of $TiO_2$, $BaCO_3$ and $CaCO_3$ or $(Ba,Ca)CO_3$, and the as-obtained powders are generally rather coarse, poorly uniform and, therefore, not meet the current trend of small size, uniform chemical composition, high chemical purity and certain morphology. In addition, the BCT powders prepared via solid-state reaction are of low solubility limit of $Ca^{2+}$. In order to achieve the high solubility of $Ca^{2+}$, BCT powders should be calcined and recalcined at a rather high temperature for several times. By contrast, many liquid processes [10] have received a particular emphasis from the viewpoint of high solubility limit, stoichiometry control, reproducibility, purity and small particle size. In recent years an increasing interest has been focused on the low temperature direct synthesis (LTDS) [11–13] of $BaTiO_3$ in aqueous medium using solution of inorganic or organo-metallic compounds at temperature <100 °C, because of their low cost and its attractive processing such as single-step process and high-yield of the anhydrous product.

To the best of our knowledge, there are no reports on preparation and properties studies of BCT via LTDS method. In this letter, we report the first LTDS-based preparation and elementary dielectric properties of BCT, and the detailed works are in progress.

For the LTDS method, a 1.0 L of batch stirred tank was used and nano-sized $BC_xT$ ($x$ = 0.05, 0.10, 0.15, 0.20, 0.30, 0.35) powders were prepared from $BaCl_2$, $CaCl_2$ and $TiCl_4$ precursors in a strong alkaline NaOH solution (6.0 mol $L^{-1}$) at 90 °C under nitrogen at ambient pressure. The excess NaOH used was to maintain a high pH value (pH > 13) throughout the reaction for achieving the complete precipitation of BCT. The total concentration of mixed chlorides in feed solution was kept at 1.0 mol $L^{-1}$, and the initial ratio of $[Ba^{2+} + Ca^{2+}]/[Ti^{4+}]$ in the mixed chorides solution was 1.07. The volume ratio between mixed chlorides solution and NaOH solution was equal to 1.0.

The fully mixed solution of chlorides and NaOH solution were respectively heated to given temperatures and then simultaneously and continuously added into the reactor, which was previously filled with a certain amount

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of NaOH solution preheated to reaction temperature. At an encountering of the above two solutions, an instantaneous formation of white precipitation was observed. The entire precipitation process lasted only 10 min. Then, the precipitations were washed, filtered, and finally dried at 80 °C over night.

The as-prepared powders were characterized by different techniques. Particle size and morphological characterization was performed via ordinary transmission microscopy techniques (TEM, Model Hitachi H-800, Cambridge, UK) and scanning electron microscope (SEM, XL-30, FEI, USA). Phase identification was conducted using an X-ray diffractometer (Shimadzu XRD-6000) with Cu K$\alpha$ radiation. A S250 MK-30 SEM equipped with a LINK AN10000 Energy-dispersive Spectroscopy (EDS) system to semiquantitatively analyze the chemical composition of the as-prepared powders. The specific surface areas were measured by a gas adsorption analyzer (Micromeritics ASAP-2010). Dielectric measurements were carried out on an automated system equipped with a temperature control box and a LCR meter (Hewlett-Packard 4192A). For studying the dielectric properties, the precalcined powders were crushed, reground and then palletized at a pressure of 2 MPa. After sintered at 1250 °C for 2 h, the above pellets were polished and electroded with Ag paste on both sides, and the capacitances were evaluated at a frequency of 1 kHz and at temperatures ranging from −55 to 200 °C.

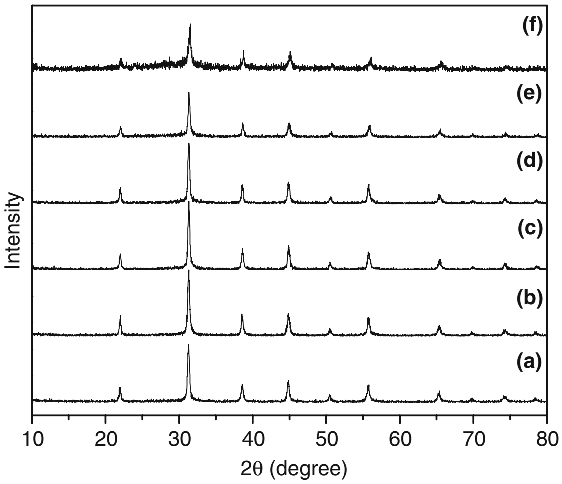


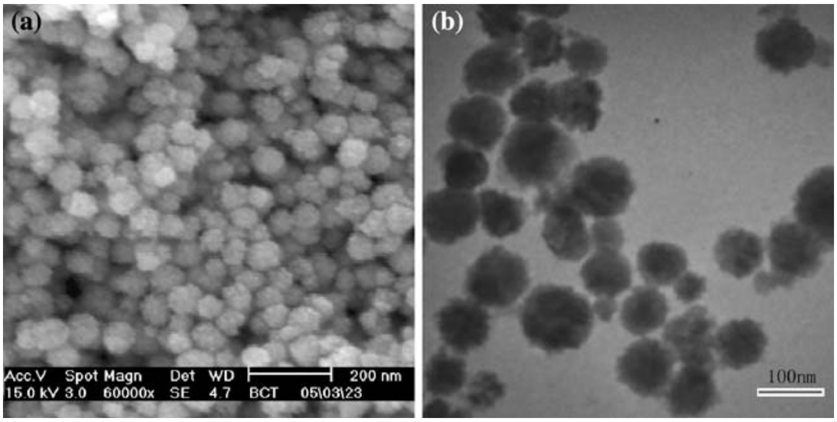
**Fig. 1** XRD pattern of BCT samples. (**a**) $BC_{0.05}T$, (**b**) $BC_{0.10}T$, (**c**) $BC_{0.15}T$, (**d**) $BC_{0.20}T$, (**e**) $BC_{0.30}T$, (**f**) $BC_{0.35}T$

XRD investigations (Fig. 1) have shown that the as-prepared powders with calcium concentration lower than 30 mol% are crystallized as single-phase BCT. Very few if any impurity peaks, such as $BaCO_3$, $CaTiO_3$, $TiO_2$ are present. The second phase is observed with further increase in calcium content up to35 mol%, suggesting that the homogeneity limit of $Ca^{2+}$ has been broadened for BCT prepared by the LTDS route. The presently observed homogeneity limit is much higher than those synthesized by solid-state reaction [3, 6–9], clearly demonstrating the advantages of LTDS technique in preparing the titanate solid solutions. While the EDS analysis gives additional evidence that barium, calcium, and titanium present in each grain, ruling out formation of $CaTiO_3$ up to 30 mol%.

Figure 2 is the TEM and SEM micrographs of some typical particles of $BC_{0.2}T$. The mean particle sizes of various $BC_xT$ are all about 70 nm, and not affected by the calcium content. The analysis for the images reveals that most of the particles are rounded single crystal particles with somewhat ‘‘knobbly’’ around the edges. The BET measurements give another confirmation that the concentration of $Ca^{2+}$ does not affect the particle size. The specific surface areas of all the as-precipitated powders are about 45 $m^2/g$.

Figure 3 presents the temperature dependence of dielectric constant and dissipation factor measured at 1 kHz for as-calcined ceramics. It is evident that as the $Ca^{2+}$ content increasing, the dielectric maximum ($\varepsilon_{max}$) decreases and broadens. The incorporation of $CaTiO_3$ by

**Fig. 2** (**a**) SEM images and (**b**) TEM images of $BC_{0.20}T$ particles



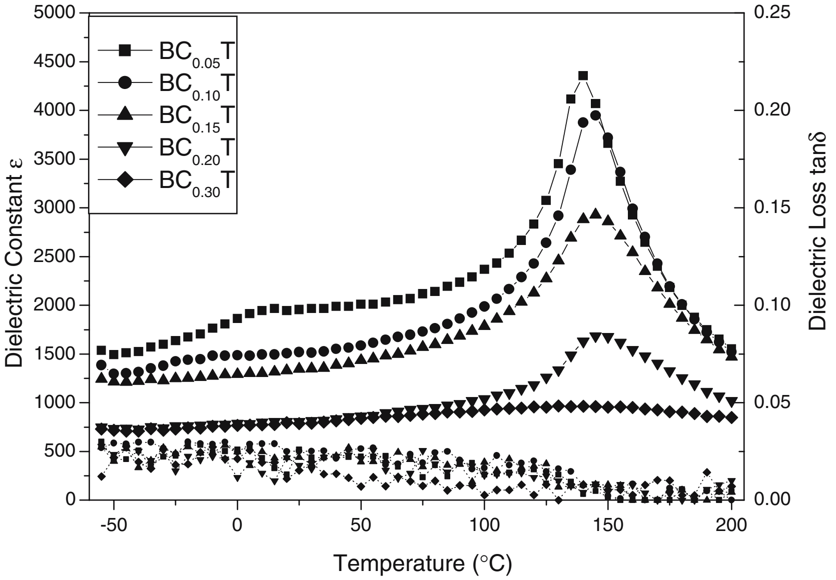


**Fig. 3** Dielectric constant and dielectric loss of BCT ceramics

the LTDS method in the range of 5–30 mol% shows an increase in Curie point to 145 °C. The dissipation factor tan *δ*, however, however, is not affected by the calcium content, and lies between 0 and 0.03 in the whole temperature range. The values of tan *δ* are lower than that of BCT powers prepared via other wet chemical routes [10].

In summary, nanosized BCT powders synthesized from the cheap raw materials via a single-step process is described. The process is extremely fast and requires a temperature as low as 90 °C at normal pressure. The process is a promising candidate for preparing high solubility limit BCT powders. The as-prepared BCT ceramics have high dielectric constants and low dissipation factors.

**Acknowledgements** This work was supported by the National Natural Science Foundation of China (Grant no. 20236020, 20325621), the Talent Training Program of the Beijing City (grant no. 9558103500), and the Fok Ying Tung Foundation (grant no. 81063).

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