

Modification of barium titanate powders for capacitor applications

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As the miniaturization with increasing functionalities and acceleration of the clock speed of electronic devices continues, the desired characteristics and processability of the starting powder become more of an issue. For barium titanate (BT) for capacitors, one is the chemical stability of BT in water as the slip medium. Aqueous processing of BT is considered to replace the current state-of-the-art non-aqueous processing technology for the obvious reasons. The second issue is the size of the particles. A greater volume efficiency of passive components, and multi-layer ceramic capacitors (MLCCs) in particular, points toward thinner dielectric layers or embedded design. All of these require a smaller particle size of the raw BT powders with closely-controlled particle morphology, high dispersibility, and better dielectric properties. This paper presents some of our recent results in meeting the demands for current and future capacitor applications of BT powders. One is in the property of the starting powder and the other is in processing of the powder for producing MLCCs. The third issue is the crystal phase of the BT particles at room temperature with the size in the range of nanometre. The fourth issue is the impurities incorporated in the BT crystal lattice. One notable impurity is hydroxyls. These issues are considered to meet the demands by modifying BT for current and future capacitor applications.

Key words: Barium titanate powder, Leaching, Nanoparticles, Passivation, Tetragonality.

Background

Barium titanate (BaTiO_3 ; BT), owing to its excellent dielectric properties, is the most widely used material for electronic capacitors. BT-based dielectrics have dominated the ceramic capacitor industry since 1950s, representing 80-90% of the business [1, 2]. With the rapid miniaturization of electronic devices, the downsizing of multilayer ceramic capacitors (MLCCs) has been accelerating. As a result, it is expected that the thickness of dielectric layers in MLCC will become less than 1 μm . Consequently, the particle size of BT powders will continuously decrease to a few tens of nm. However, in ferroelectric fine particles, it was known that ferroelectricity decreases with decreasing particle and grain sizes, and disappears below a certain critical size; so called the "size effect" in ferroelectrics [3-9]. The preferred tetragonal phase of BT may be unstable at room temperature for a crystallite size below a certain size and then the stable phase is cubic. Therefore, the size effect in ferroelectrics such as BT can be considered to be one of the most important phenomena for an interest to the industry as well as to the scientific community. Some researchers have estimated the critical size to be around 30-100 nm in BT fine particles [10-12]. The preferred tetragonal phase of BT can be identified by x-ray diffractometry

(XRD). Venigalla [13] showed the size limit to distinguish the tetragonal phase from the cubic phase is ~ 200 nm by using XRD peak splitting of (002) and (200) at $2\theta = 45^\circ$. Below this size, the BT particles will appear cubic phase under XRD examination. We define this as tetragonality or c/a ratio of BT crystal lattice. We have shown that the phase change from cubic to tetragonal depending on the crystallite size is a gradual transition with the increase in c/a ratio and there is no one critical size dividing the phases [14].

Despite the well known chemical instability of BT in water [15, 16], aqueous processing of BT needs to replace the current state-of-the-art non-aqueous processing technology for the obvious reasons. The instability of BT in water affecting the dispersion exhibited in an adverse manner is caused by the preferential leaching of barium cations from the BT lattice. This behavior will affect the dispersibility and the Ba/Ti compositional ratio in the final product [16-19]. In order to use a water-based slip system in the MLCC industry with greater reliability, we have adopted a passivating agent layer (PAL) on BT particle surfaces to reduce the Ba^{2+} leaching. The PAL is also used as a dispersant to stabilize the particles in the water medium [19].

Re-dispersible spherical BT nanoparticles with a narrow size distribution with a lower hydroxyl content were produced by our novel method to produce pure crystalline nanometre sized BT called the Ambient Condition Sol (ACS) process [20-22]. Controlled particle size with a uniform distribution in the size range of 50-100 nm for a different refluxing medium was produced

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rapidly. During the process, a polymeric surface modifier can be added to protect the surface from agglomeration and to provide improved dispersibility after drying.

Modern electronics of advanced electronic packaging applications, such as integral decoupling capacitors and tunable RF filters, will require embedded capacitors with a superior performance. Conventionally, discrete components are mounted onto a printed circuit board (PCB) or interconnected substrate. This results in higher parasitic capacitance, lower reliability, and large attachment area requirements [23]. Growing demand for faster clock speed, miniaturization, and higher volumetric efficiency of MLCCs is leading the trend toward embedded passive components in system on packaging (SOP) [24-26]. In one of the efforts, high dielectric constant (K) BT particles of $\sim 0.2 \mu\text{m}$ were dispersed in a polymer matrix, e.g., epoxy resin. This composite structure yielded the highest K of meager ~ 150 at as high as 85 vol% ceramic content, with poor mechanical properties of the PCB, and dispersion difficulty of the ceramic particles in the polymer matrix [27, 28]. The results are unsuitable for the next generation high performance electronic devices. The reasons for the unimpressive results are thought to be: 1) BT powder was predominantly cubic phase, i.e., low tetragonality, 2) the particle size is too large requiring so high ceramic loading, and 3) the imperfect dispersion of the particles in the matrix. Some of commercially-advertised embedded capacitors [23] have even lower K. The K needs to be increased.

Barium Ion Leaching

Using Cabot's hydrothermal BT-8 powder (Cabot Performance Materials, Boyertown, PA) of a specific surface area of $8.5 \text{ m}^2/\text{g}$, a Ba/Ti ratio of 0.998 and a median particle size of $0.24 \mu\text{m}$, 0.5 wt% PAL was added to observe the effect of a PAL on the kinetics of the Ba^{2+} leaching at different aging times up to 96 hr. The organic PALs used are listed in Table 1.

Ba^{2+} leaching, monitored by the EDTA titration method [18], at pH=8 and room temperature as a function of aging time is quite high in the first few minutes of

Table 1. List of organic passivation agents and their structural names

KD-6:	copolymer of methylmethacrylate backbone with polyethylene glycol side chains
APA:	ammonium polyacrylate
PAsA-Na:	polyaspartic acid – sodium salt
Oxalic acid:	$(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$
Citric acid:	$\text{HOCCOOH}(\text{CH}_2\text{COOH})_2 \cdot 2\text{H}_2\text{O}$
PAMPA-MA:	co-polymer of 2-acrylamido-2-methyl propane-sulfonic acid with maleic anhydride

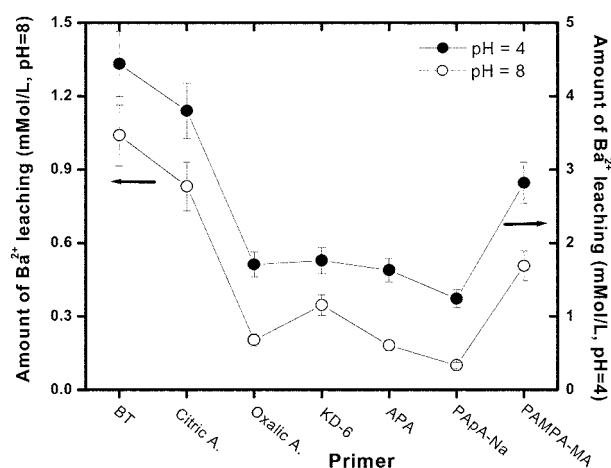


Fig. 1. Effect of organic passivating agents on Ba^{2+} leaching at pH 4 and 8 after 2 days aging.

aging. Blanco-Lopez *et al.* [29] also reported Ba^{2+} ion leaching in water occurring quickly and little Ba^{2+} ion concentration change after several hours. The effects of organic adsorbates, i.e., PAL or primer, on the passivation of Ba^{2+} ions leaching at pH 4 and 8 for 2 days are presented in Fig. 1. After mixing the BT powder with 0.5 wt% PAL or primer, this slurry was dried instantly at 120°C for 12 hours to make a PAL-coated BT powder. The number of Ba^{2+} ions leaching clearly reduced with the PALs and showed 3-5 times less leaching than without a PAL.

For KD-6 shown as an effective PAL, Fig. 2 demonstrates the effect of Ba^{2+} ion in the slip as shown by SEM microstructures of BT slips with and without the

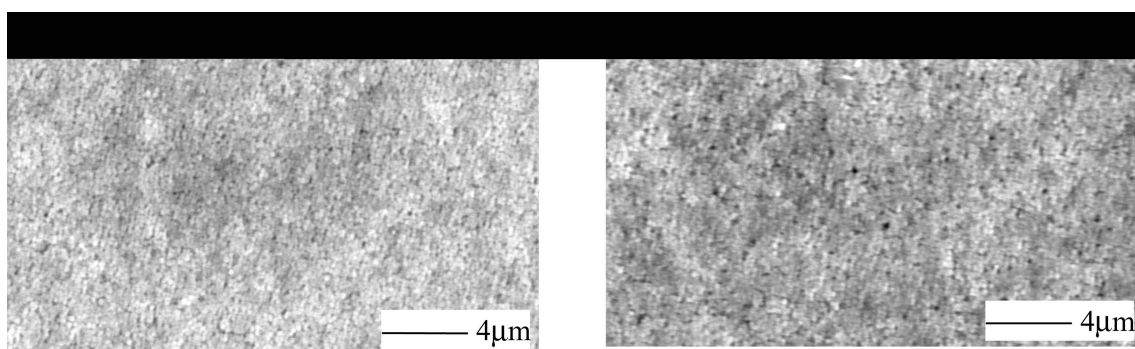


Fig. 2. BT powder dispersed in water with KD-6 without additional Ba^{2+} ions (A) and with 1 mol% Ba^{2+} addition (B).

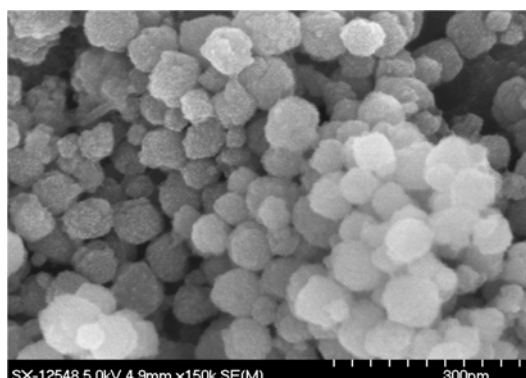


Fig. 3. Redispersible ACS BT prepared with APA.

excess Ba^{2+} ion added as barium hydroxide. A poorer microstructure with increased porosity is the result due to the presence of Ba^{2+} ions in the slip. Therefore, it is desirable to keep the Ba^{2+} concentration minimum in the slip medium. This could be achieved by introducing a PAL.

Nanometer Sized Re-dispersible BT Particles

In the nanoparticle BT synthesis by the ACS process [20–22], BT nanoparticle nuclei are formed from water-soluble chemical precursor gel, e.g., barium chloride and titanium tetrachloride, but the growth takes place in another liquid medium under refluxing for 1–5 hr. For the re-dispersible nano-BT particles, 0.5 wt% ammonium polyacrylate (APA) was added to the water medium just prior to the refluxing process. The APA can also contribute to reducing the barium ion leaching as a PAL. An SEM micrograph of the particles is shown in Fig. 3. The redispersibility of the particles was tested by drying the powder in a vacuum oven at 70°C followed by dispersing the dried powder in water by 10 minutes ultrasonication. Particle size measurements were

then made by a dynamic light scattering (DLS) technique. The redispersibility of the dried nanoparticle BT in terms of the particle size was compared with the particle size before drying. The mean particle sizes differ by less than 10% as shown in Fig. 4. The procedure has shown to be effective for drying wet BT particles without an adverse effect on the subsequent redispersion in the nanometre size range.

Tetragonal Nanoparticles

The room temperature XRD patterns of ACS BT showed cubic phase crystalline BT formed at 20 minutes after the start of the refluxing reaction. However, a Raman spectroscopy examination revealed the ACS BT having some tetragonality as was the case in our redispersible hydrothermal BT [30]. These XRD pure cubic BT powders of 100 nm in particle diameter coated with an organic layer may be useful for embedded capacitors for enhanced dispersibility in the polymer matrix of choice for PCB. Since the as-synthesized BT of nanometre range exhibits low tetragonality due to the critical size limit for tetragonal phase [13], it is desired to increase the tetragonality at the size range. The question on the “XRD tetragonality” discussed earlier was examined by treating a “XRD cubic” phase BT chemically and physically [31]. The powder used for this experiment was the same BT-8 having a mean particle size of 240 nm as in the barium ion leaching experiment. Here the chemical treatment was carried out by placing the cubic BT powder in dimethylformamide at 170°C for 6h under a sealed condition. The physical treatment consisted of exposing the cubic BT powder to a custom-designed 2.45 GHz microwave at 3 kW with the temperature monitoring by a 2-color pyrometer.

Figure 5 shows the XRD patterns for a cubic BT powder before and after treating chemically. It is clear

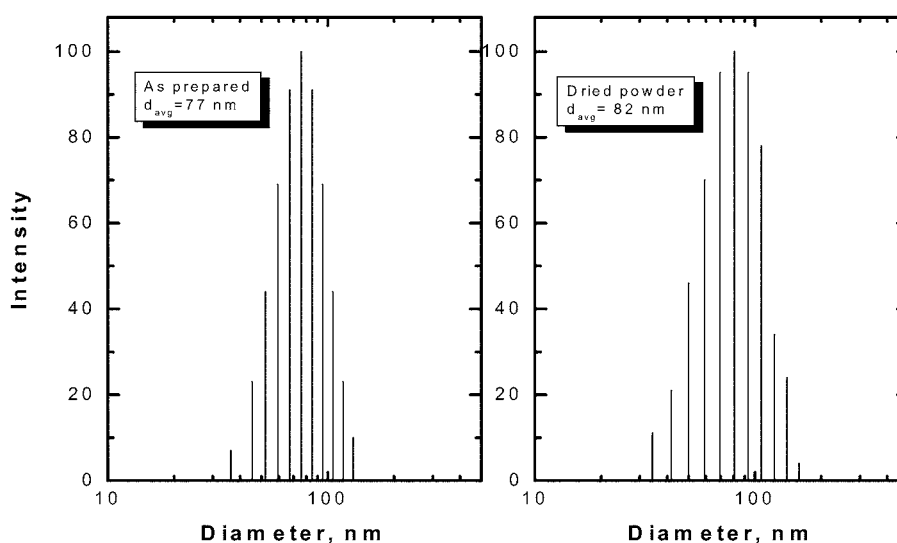


Fig. 4. DLS particle size distribution of ACSBT dispersed in water before and after drying.

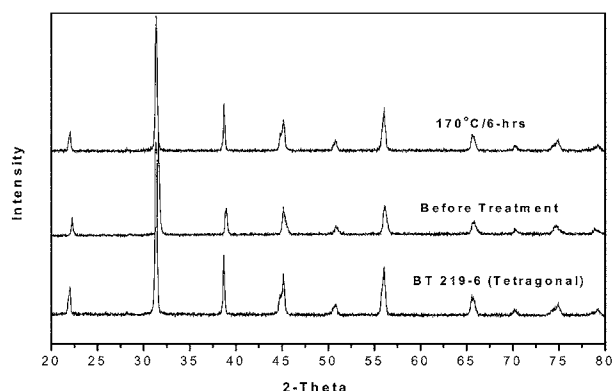


Fig. 5. XRD patterns of BT-8 powders before and after chemical treatment. BT 219-6, which is a commercially known tetragonal BT, is shown as a reference.

that the cubic phase BT transformed to tetragonal as shown by the doublet peaks at $2\theta = 45^\circ$ for (002) and (200). Did this happen by the growth of the crystallite size? Fig. 6. shows the particle morphology before and after the chemical treatment. The particle morphology appeared to be unchanged. The particle size determined by DLS and the BET surface area measurements revealed that the particle size and the surface area decreased slightly by the chemical treatment. The differential scanning calorimetry (DSC) in Fig. 7 shows the change in the Curie transition peak due to the tetragonal-to-cubic phase transition. Before the treatment, the BT was cubic and hence there was no ΔH

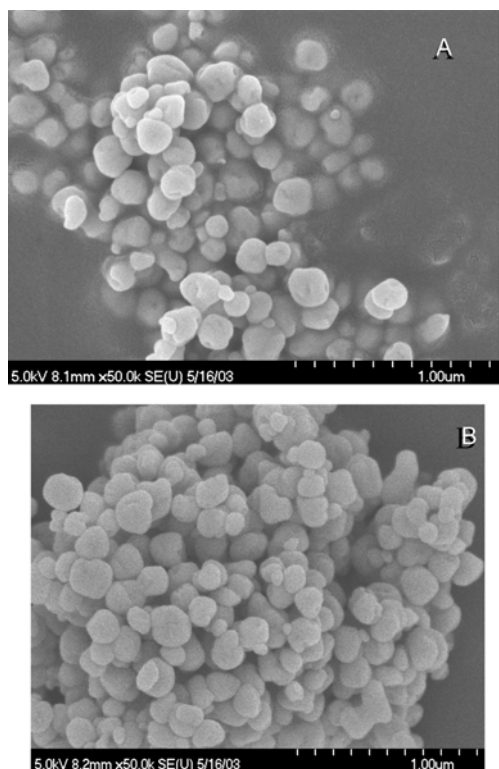


Fig. 6. SEM micrographs of BT-8 before chemical treatment (A) and after treatment (B) for 6 hr at 170°C.

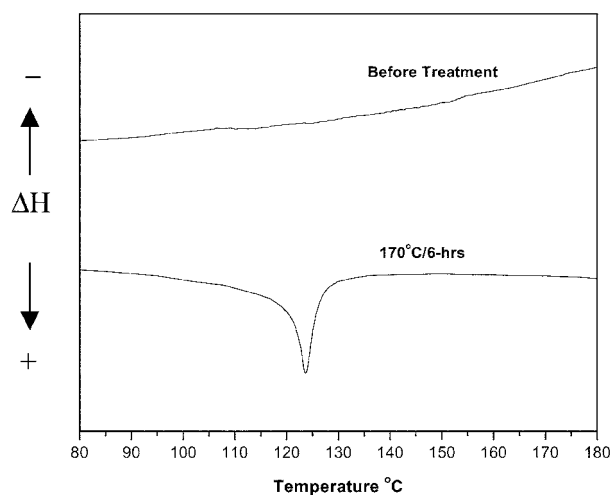


Fig. 7. DSC of BT-08 before and after chemical treatment.

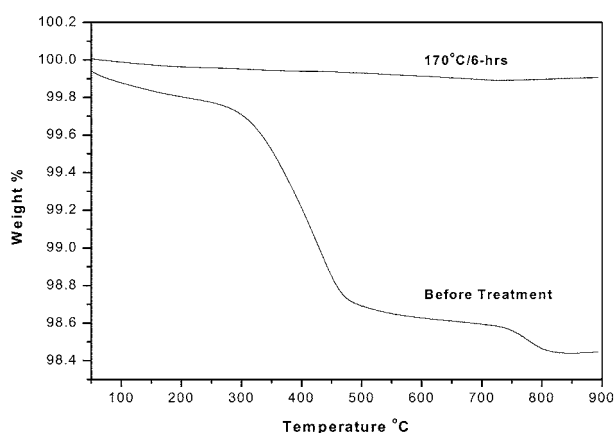


Fig. 8. TGA of BT-8 powder before and after chemical treatment.

endothermic DSC peak at the Curie point due to the tetragonal to cubic transition as the temperature was raised from room temperature to 180°C. How did this happen? Thermogravimetry shown in Fig. 8 exhibits ~1% weight loss due to water or hydroxyl, mostly from the BT crystal lattice in the temperature range of 300–400°C before the treatment and essentially no weight loss after the treatment. Therefore, the cubic-to-tetragonal transition may have been promoted by the elimination of the lattice protons, as suggested by Hennings *et al.* [32], without the growth of the grain size. The quantitative analysis of these proton impurities in the BT lattice is currently under investigation.

Microwave treatment of a cubic phase BT powder yielded tetragonal phase as shown by the XRD in Fig. 9. The corresponding DSC thermogram supports the transformation by the microwave exposure. SEM micrographs suggested that significant sintering begins at $t > 10$ minutes at 1250°C microwave exposure, but the cubic to tetragonal transformation began at ~5 minutes exposure. The narrow window of tetragonal transformation time is being investigated and will be reported later [33].

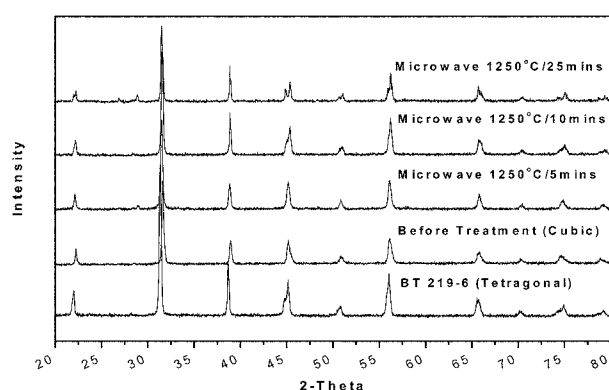


Fig. 9. XRD of microwave treated BT-8 before and after the exposure. BT 219-6, a known tetragonal BT, is shown as a reference.

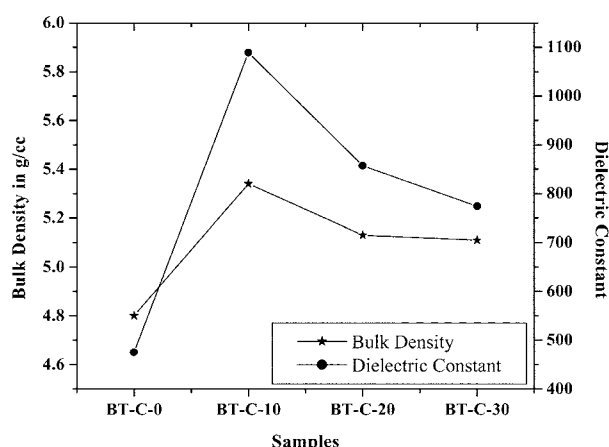


Fig. 10. Bulk density and dielectric constant profile for Cabot BT-08 and silver composites.

Enhancement of K

Can the K of BT with particle size <100 nm be increased? As stated earlier in the background section, the K values need to be higher for embedded capacitor applications. The K values of BT-8 powders treated chemically (shown in Fig. 6B) were measured by using an HP LCR meter and compared with the untreated BT-8 powder. Our preliminary results show ~2X increase in the value by the treatment supporting the property of tetragonal phase BT as compared with cubic phase (Fig. 6A).

Efros and Shklovskii [34] prepared a composite material consisting of a randomly distributed conducting phase in a dielectric matrix. The metal-nonmetal transition takes place when the volume fraction of the conducting phase approaches the percolation threshold. Wilkinson *et al.* [35] reported the enhancement of K near the percolation threshold when one of the components of a mixture of two materials is a conductor.

BT-8 powder was blended with silver nitrate solution for different weight % loadings of silver nitrate at 0, 10, 20, and 30 followed by drying and calcining. The

blended powder was cold pressed into BT/Ag composite pellets for sintering and property measurements. Fig. 10 shows the K values of BT as a function of silver content after sintering at 1150°C. There is 2-3X increase in the K simultaneously with the bulk density. Although the addition of silver enhanced the sintering, the increase in the K is not only caused by the increase in the bulk density as supported by our calculation of theoretical density and measured density of the composites. Considering the theoretical density of BT (6.01 g/cm³) and that of silver (10.5 g/cm³), the bulk density increase is from the increase in the silver content. We are currently applying the results into the ACS BT synthesis. These results are expected to be useful for embedded capacitor by dispersing the BT/Ag powder well in a polymer matrix.

Conclusions

The surface coating by organic passivation agents is effective in reducing Ba²⁺ ion leaching. BT nanocrystals and redispersible particles can be formed in different liquid media under an ambient condition. These nanocrystals were identified as meta-stable cubic phase BT by XRD with some tetragonality. Tetragonality can be increased by a chemical treatment of a cubic phase BT. Microwave treatment is also effective in converting a cubic phase BT to tetragonal phase BT powder. K of a BT was enhanced 2-3X by incorporating a conducting phase silver. These modifications are expected to be useful for the new embedded capacitors.

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