

Aqueous processing of barium titanate powders

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In many modern electronic devices, multi-layer ceramic capacitors (MLCCs) are used in large quantities. For a greater volume efficiency of MLCCs, current efforts include thinner dielectric layers and a larger number of layers in a given volume, together with embedded-capacitor design. All of these require a smaller particle size of the raw ceramic material, barium titanate (BaTiO_3) powders, with closely controlled particle morphology and processing behavior. The current state-of-the-art technology for MLCCs utilize non-aqueous or solvent-based processing. For a cleaner environment and a greater cost effectiveness of the processing, development of water-based processing technology for MLCCs is more imperative than ever. As the miniaturization of electronic devices continues to demand smaller particle size powders with controlled morphology, the desired characteristics of the starting powder becomes a critical issue. Among the methods to produce sub-micrometer BaTiO_3 powder (BT), hydrothermal synthesis has been shown to have an edge. However, hydrothermal BT is expensive and exhibits sintering problems due to the large amount of lattice hydroxyls which were incorporated during its aqueous-based synthesis process. A new synthetic method; Ambient Condition Sol (ACS) process has been considered in our laboratory which is to decrease the amount of incorporated hydroxyl ions in a water-free synthetic medium. The increasing difficulty of dispersion and stability of nanometer-sized BT particles is mitigated by introducing a steric barrier layer during the ACS synthesis, resulting in a re-dispersible particles in water. This concept was further demonstrated in the surface passivation of BT particles in water by reducing the Ba^{2+} ion leaching over an extended period of time. The results showed the Ba^{2+} leaching rate to be an inverse function of the solution pH and a direct function of the organic adsorption isotherm onto the BaTiO_3 surface. The effectiveness of organic passivation agents was directly proportional to the pH of the medium. The BT particle morphology, degree of passivation, evidence of lower concentration of lattice hydroxyl impurity, the kinetics of ACS synthesis for BT, redispersibility, and the resulting phase analyses are reported.

Key words: barium titanate, surface passivation, nanoparticles, multilayer capacitors, ion leaching, refluxing.

Introduction

Multi-layer ceramic capacitors (MLCCs) consist of alternating layers of dielectric materials and internal metal electrodes. The dielectric layers are generally produced by tape casting, starting from a fine powder of barium titanate (BT) suspended in a liquid medium [1, 2]. Hence, understanding of the powder characteristics and behavior in liquid media are prerequisites for success in MLCC processing. As information technology accompanied with continuing miniaturization of electronic devices increases, better controlled/designed starting materials are needed. Currently "perfect" BT powders in the nanometer size range are not available commercially. Agglomerates are always present in as-received fine powders and must be removed to enhance densification and microstructural homogeneity. While lowering the sintering temperature is important for preparing all technical ceramics, it is of special concern for co-firing of ceramics with base-metal electrodes

(BME) as required in current MLCCs.

For a cleaner environment and a greater cost effectiveness of the processing, use of water as the processing medium for suspending the fine BT particles makes more sense for MLCCs and is more imperative than ever. Our recent results [3, 4] indicate that the microstructure of the best BT tape from aqueous suspensions before firing is inferior to the same BT tape microstructure from nonaqueous media as shown in Fig. 1. The aqueous dispersion of BT needs to be improved to match that of the nonaqueous. Efforts have been made in industry to switch some nonaqueous systems to aqueous processing [5, 6]. Nevertheless, the changes have been slow or only partially successful because the fundamental science of aqueous powder processing of this type of ceramics has not yet been well understood. It has been found that barium ions leaching out from BT not only introduce structural inhomogeneity but also gives difficulties in dispersion [7-10]. The leached Ba^{2+} from the BT surface can interact in an adverse manner with other organic additives [11-13]. The Ba^{2+} ions present in the medium can cause the folding of the chains in the polymeric additives caused by a salting-out mechanism. This folding will impair not only the homogeneous dispersion of BT particles but also lead

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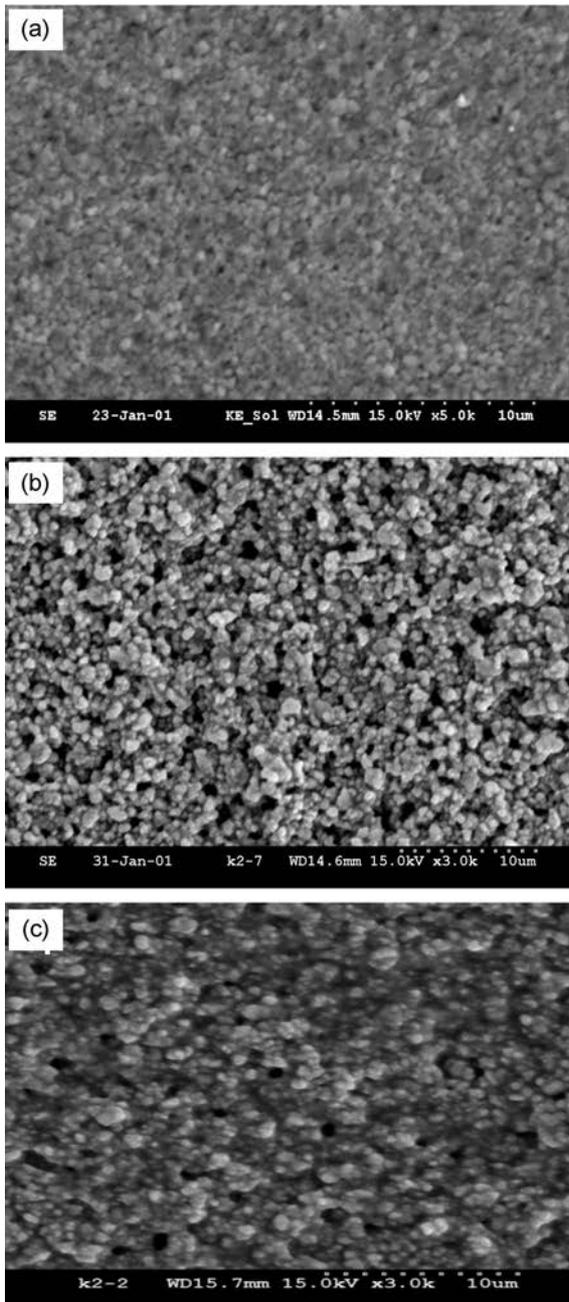


Fig. 1. SEM micrographs of X7R BT green tapes @3000X; (a) nonaqueous, showing uniform dispersion of the particles, (b) aqueous tape from a polyacrylate dispersant and latex binder showing some particle agglomeration and pores, (c) Clemson's aqueous green tape fabricated with a copolymer of polyethylene glycol/polymethacrylate.

to the creation of defective holes in the fired tapes as a result of the burnout of the salted-out polymers. In order to use a water-based slip system in the MLCC industry with greater reliability, understanding and controlling the Ba^{2+} leaching are essential. To overcome this we have introduced a passivating agent layer (PAL) on to the BT surface to reduce the leaching of barium ions. The PAL is also used as a dispersant to stabilize the particles in the water medium.

Among the methods recognized as producing sub-micrometer or nanosize BT, the hydrothermal technique has been considered to have an edge. The powder resulting from this exhibits submicrometer or nanometer size with a uniform geometry and narrow size distribution. It is, however, difficult to dry without causing agglomeration. We have overcome this problem by introducing a steric barrier layer (SBL) of an organic dispersant to the precursor sol during the hydrothermal treatment [14-18]. This yielded a redispersible spherical nanoparticle BT with a narrow size distribution.

Hydrothermal BT powders, in addition, have shown a sintering problem due to the hydroxyls in the oxygen sublattice, and MLCC industry is reluctant to use this BT powder [6]. Therefore, we have developed a novel method to produce pure crystalline BT in the size range of 40-100 nm at ambient pressure and temperature, called the Ambient Condition Sol (ACS) process [19, 20]. The revolutionary aspect of this method is that the process does not require high temperature and pressure to crystallize BT of a controlled particle size with a uniform distribution. Since this is done in a hot organic liquid medium, it is expected that the hydroxyls in the lattice causing the sintering problems in the hydrothermal BTs may be avoided or minimized [20-22].

Experimental

For the leaching study, Cabot's hydrothermal BT-8 powder (Cabot Performance Materials, Boyertown, PA) having a specific surface area of $7.8 \text{ m}^2/\text{g}$, a Ba/Ti ratio of 0.998 and a median particle size of $0.17 \mu\text{m}$ was used. To study the extent of Ba^{2+} ions leaching from the BT, 6 g of BT-8 powder were dispersed in 24 ml of deionized water, corresponding to 4.2 vol. % of the BT powder. NH_4OH and CH_3COOH were used to adjust the solution pH. After being aged for the desired length of time, the slurry of BT was centrifuged for 30 min followed by taking a 12 ml aliquote of the supernatant diluted to 50 ml with deionized water, and adjusting the pH to 12 with 10 M KOH solution. The solution was titrated with 0.001 M EDTA solution using a Mettler Titration Meter (DL50 Titrator, Mettler Toledo, Switzerland). In some samples, 0.5 wt% organic agents were added to observe the effect of the surface-active organic additives or PALs on the kinetics of the Ba^{2+} leaching at different aging times up to 96 hr. The organic PALs

Table 1. List of organic agents and their structural names

KD-6:	(acrylic graft copolymer+polyethylene glycol)
Tween 80:	(polyoxyethylene(20) sorbitan monooleate)
Darvan C:	(ammonium polymethacrylate)
APA:	(ammonium polyacrylate)
PAsA-Na:	(polyaspartic acid-sodium salt)
Oxalic acid:	$(COOH)_2 \cdot 2H_2O$:
Citric acid:	$HOCCOOH(CH_2COOH)_2 \cdot 2H_2O$

used are listed in Table 1. The effects of heat treatment were examined by heat treating the BT-8 powder at 400-1000°C for 2 hours in air to remove the surface-adsorbed species, Fourier transform infrared (FT-IR) spectra of each sample were taken using a diffuse reflectance stage with a resolution of 4 cm⁻¹.

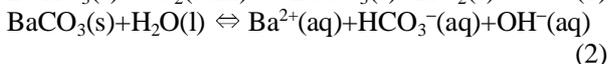
In the nanoparticle BT synthesis via the ACS process [20, 22, 23], BT nanoparticle nuclei were formed from water-soluble chemical precursors but the growth takes place in an organic liquid medium under a refluxing condition. The starting materials used for this were barium chloride (99.6% BaCl₂·2H₂O, Fisher Scientific), and titanium tetrachloride (99.6% TiCl₄, Alfa Aesar). An aqueous solution of barium and titanium was obtained by mixing 21.99 g BaCl₂·2H₂O in 90 ml deionized water and 11.38 g TiCl₄ in 15 ml concentrated HCl. The Ba/Ti ratio in the solution was 1.5:1. The solution pH was then adjusted to 14 by 10 M KOH. The precursor slurry was then transferred into different liquid media in a glass flask heated in an oil bath under magnetic stirring and refluxing. A small amount of samples (20 ml each) were taken from the flask at different time intervals up to 360 min. Each sample was subject to particle size measurement and the remaining was centrifuged and washed with dilute acetic acid and water, followed by drying in an oven at 80°C overnight.

For the redispersible nano BT particles, 0.5-1 wt% hydroxypropyl cellulose was added to the water medium just prior to the refluxing process. 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 min ultrasonication and particle size measurements were then made by a dynamic light scattering (DLS) technique.

Room temperature XRD (RTXRD, Scintag PAD V using CuK_α with λ=0.15406 nm) was used to check for crystallinity and to measure crystallite size by the XRD peak broadening and Scherrer Eqn. using the (200) XRD peak. The particle size, crystallinity, and morphology of the resulting powders were analyzed by TEM (Hitachi HF-2000), by placing the BT particles in isopropanol, on a copper grid.

Results and Discussion

In the behavior of BT particles in water, the role of CO₂ and BaCO₃ is of fundamental importance. According to the reported thermodynamic calculation [24], the formation of BaCO₃ by the reaction of BT and CO₂ is favored in air. Therefore, the two possible reactions affecting Ba²⁺ leaching are:



By combining the reaction eqns. (1) and (2), one can

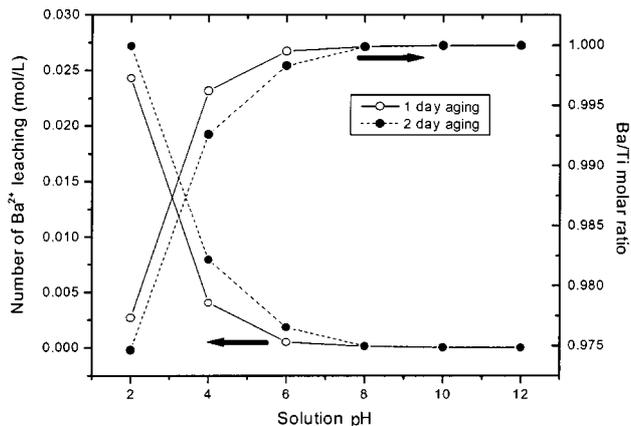


Fig. 2. Number of Ba²⁺ ions leaching and the resultant Ba/Ti molar ratio of Cabot's BT-8 as a function of the solution pH.

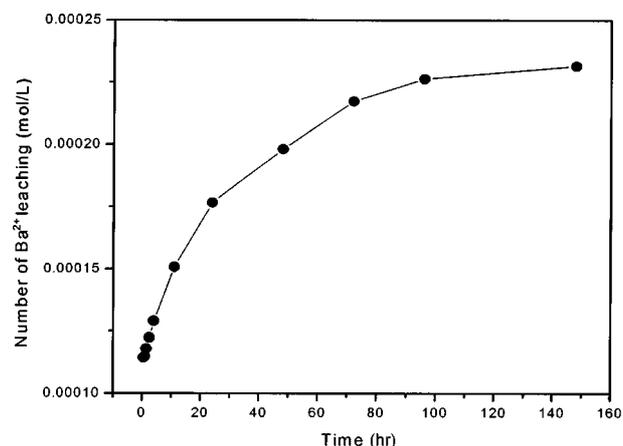


Fig. 3. The number of Ba²⁺ ions leaching vs. time at pH=8 and at room temperature.

expect appreciable Ba²⁺ leaching in water unless the partial pressure of CO₂ is extremely low. By contrast, TiO₂(s) is generally regarded as insoluble in water [25, 26]. Therefore it is likely that Ba²⁺ will be released from the BT surface until the surface becomes "TiO₂-like". At a lower pH the equilibrium in eqn. (2) will shift to the right as the OH⁻ ions are consumed by the low pH which results in increased solubility of BT in water. The results of this along with the corresponding Ba/Ti ratio of the BT sample as a function of pH are shown in Fig. 2.

Figure 3 shows the Ba²⁺ leaching behavior at pH=8 and at room temperature as a function of aging time. The number of Ba²⁺ ion leaching is quite high for the first measurement at 30 min of aging. After 30 min, the leaching rate gradually decreases reaching a plateau at a time greater than 100 hrs. These results on the time-dependent behavior of Ba²⁺ leaching in water have been reported by others vary markedly. Neubrand *et al.* [27] observed an instantaneous increase of Ba²⁺ ion leaching in water within the first few minutes and then a gradual decrease at a pH of 10. They explained this finding as a re-adsorption of Ba²⁺ ions onto the hydrat-

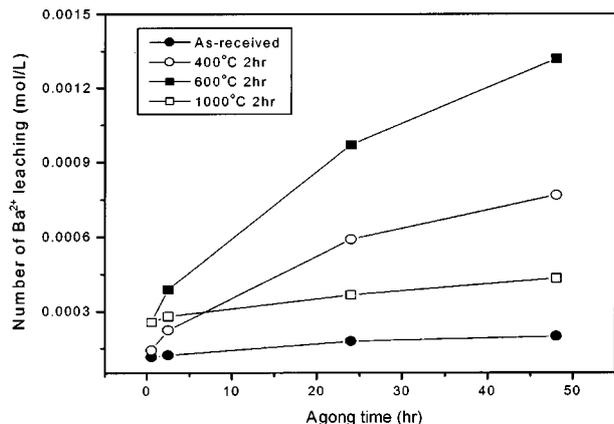


Fig. 4. Effect of heat treatment of Cabot's BT-8 powder on Ba²⁺ ions leaching rate at room temperature.

ed BT surface. On the other hand, Blanco-Lopez *et al.* [28] observed a gradual increase in the number of Ba²⁺ ion leaching in water at pH of 4 within 5 hrs of aging, after an instantaneous increase at the beginning which agrees with our results. Utech [29] explained that Ba²⁺ ion leaching in water at pH 8, 10 and 12 occurred instantaneously, reaching a steady-state within 5 minutes, *i.e.*, no Ba²⁺ ion concentration change after 5 minutes. Regarding the number of Ba²⁺ ion leaching, the average leached Ba²⁺ ion concentration in our experiment lies between the results of Neubrand *et al.*'s [27] and Utech's [29]. These discrepancies must be caused by the use of different BT powders and the uncontrolled concentration of CO₂ in the water and in the ambient air.

Pre-heat treatment of Cabot's BT-8 powder in air increased the number of Ba²⁺ ion leaching as shown in Fig. 4 with the most Ba²⁺ ions leaching at 600°C and then a decrease at 1000°C. This result can not be explained by the specific surface area change since there was little change in the surface area below 600

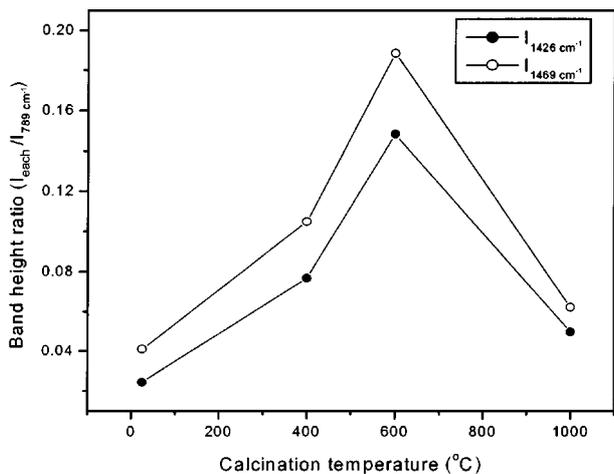


Fig. 5. Normalized carbonate band height ratios at 1426 and 1469 cm⁻¹ after heat-treatment of BT at different temperature in air for 2 hr.

°C. By increasing the pre-heat treatment temperature above 600°C, the specific surface area is decreased, and the particle size increased. The next possible variable may be the surface BaCO₃ on Ba²⁺ ion leaching. The FT-IR spectra of these powders taken within 10 min of the heat treatment indicated band height differences at ~3400 and 1200~1500 cm⁻¹. According to previous research [30-32], the broad IR band of ~3383 cm⁻¹ is attributed to the surface adsorbed water, of 1426 and 1469 cm⁻¹ to carbonates, and of 785 and 475 cm⁻¹ to BT. Semi-quantitative comparison of these species by band intensity calculated using the ratios of the band intensity caused by the species divided by the band intensity of BT at 785 cm⁻¹ showed an increasing carbonate band height, peaking at 600°C as shown in Fig. 5. This can be explained by the reaction between the atmospheric carbon dioxide and the hydroxyl ion (OH⁻) diffusing out to the BT surface which had been incorporated into the lattice during the hydrothermal synthesis of this powder. According to Hennings *et al.* [33], there is an appreciable amount of lattice-incorporated protons and hydroxyl ions (~0.4 mol/mol BT) present in hydrothermally synthesized BT powders. This OH⁻ diffused to the BT surface by annealing up to 800°C. The band height curves for hydroxyls correlated very well with the curve for carbonates shown in Fig. 5. These observations indicate that Ba²⁺ ion leaching depends more on the amount of surface carbonates than

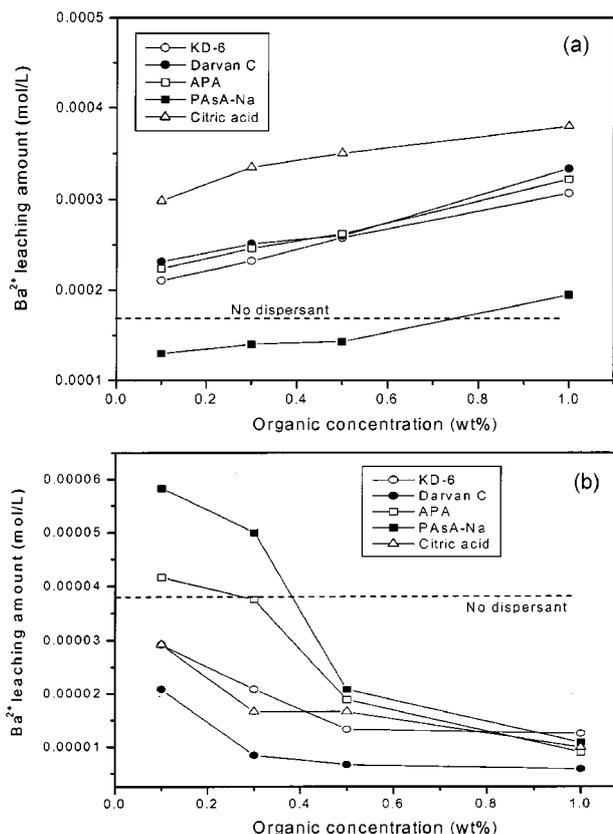


Fig. 6. Effect of organic passivating agents on Ba²⁺ leaching at (a) pH=8 and (b) pH=12 after 2 days aging.

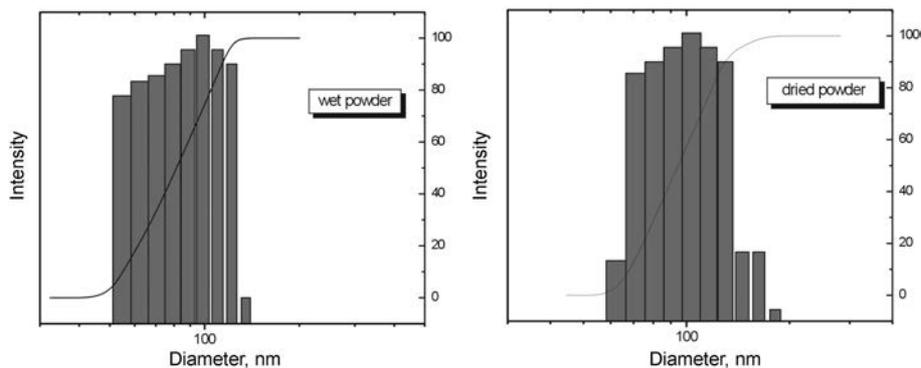


Fig. 7. Redispersibility of dried ACS BT particles expressed in particle size after dispersed in water by 10 min ultrasonication.

on the diffusion of the lattice Ba^{2+} ion with the pre-heat treated BT powders. As the temperature increased up to 600°C , the BT surface in contact with the atmospheric CO_2 formed carbonates which are soluble in water. Evidently, this form of carbonate has no ability as a PAL for Ba^{2+} ion leaching.

The effects of organic adsorbate species on passivation of Ba^{2+} ions leaching are presented in Fig. 6 for $\text{pH}=8$ (a) and $\text{pH}=12$ (b) after 2 days of leaching. In general, the number of Ba^{2+} ions leaching increased as the concentration of the organic agent increased and exceeded that of the sample without the organic additives at $\text{pH}=8$ with the exception of polyaspaltate. At the lower pH of 8, the PALs added to the Ba^{2+} solution chelated Ba^{2+} ions, shifting the dissolution equilibrium towards more leaching of Ba^{2+} ions. At $\text{pH}=12$, on the other hand, the number of Ba^{2+} ions leaching gradually decreased with the organic PAL concentration increase and showed 2~4 times less leaching than with no PALs or “dispersant.” At this higher pH, the PALs adsorbed onto the BT surface preferentially to chelate Ba^{2+} ions. Another contributing factor affecting the pH dependency of Ba^{2+} ion leaching with the PALs may be the morphology and/or conformation of the adsorbed PALs [34]. The morphology and/or conformation of the organic adsorbates at $\text{pH}=8$ may not have been conducive to passivating the BT surface from leaching, hence making the BT more susceptible to Ba^{2+} ion leaching.

For smaller size BTs with superior stoichiometry and dispersion behavior in water, we synthesized submicrometer crystalline BT powders at a low enough temperature to possess a built-in organic dispersant which acted as an SBL for the particle growth control. This was only possible with our hydrothermal or ACS processes. The redispersibility of the dried nanoparticle BT is shown in Fig. 7 in terms of the particle size as compared with the particle size before drying. The mean particle sizes differ by about 15% which is considered to be good for the size in this submicrometer range and the mild deagglomeration procedure used in this test. A sedimentation rate test and the viscosity as a function of shear rate of our BT at 40 wt% also exhibited excellent behavior as compared with TPL's nano BT

Table 2. Reaction time, temperature and size at each sampling point

Sample number	Reaction time (min)	Temperature ($^\circ\text{C}$)	Crystallite size (nm)	Average Particle size (nm)
			XRD	DLS
1	0	RT	—	322
2	5	<40	—	321
3	10	50	—	297
4	15	75	—	221
5	20	100	62.5 ± 1.7	113
6	25	102	62.6 ± 2.0	113
7	30	102	61.2 ± 1.8	118
8	60	102	60.9 ± 1.8	126
9	180	102	58.4 ± 1.8	135
10	360	102	58.6 ± 1.7	137

(mean size=50 nm) and Ticon F (submicrometer size BT by Ferro Corp.). The ACS method allowed the *in situ* sampling for particle characterization in growth and crystallization. The results are given in Table 2.

Figure 8 shows XRD diffractograms of BT crystallized in different liquids and the corresponding SEM particle and crystallite sizes in Table 3. The as-synthesized BT particles are shown to be pure cubic phase BT by XRD as well as by Raman spectroscopy. It appears that the SEM particle size is related to the dielectric

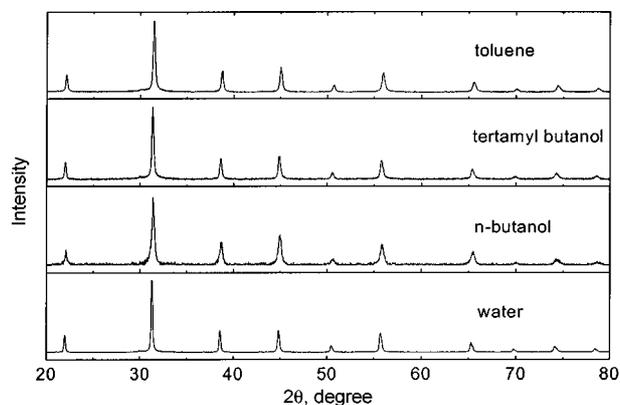


Fig. 8. RTXRD patterns of BaTiO_3 powders prepared in various media.

Table 3. ACS BT particles sizes in nanometer estimated from SEM and XRD Crystallite size of BT particles prepared in different media

Media	Toluene	n-butanol	Tert-amyl alcohol	Water
Reaction temp., °C	112	118	101	102
Crystallite size, nm	40.2±3.5	42.5±1.8	41.6±2.6	51.5±1.5
Particle size, nm	39.3±1.4	55.2±1.4	45. ±1.7	66.7±1.1

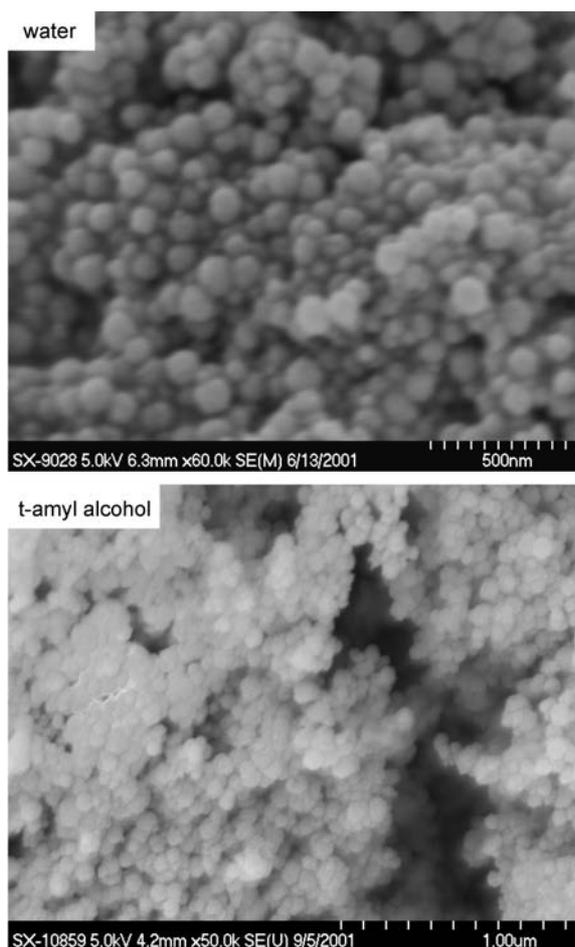


Fig. 9. SEM micrographs of ACS BTs prepared in water and t-amyl alcohol.

constant of the liquid medium, i.e., the lower the dielectric constant, the smaller the SEM particle size. This may be caused by the difference in the surface tension and electrostatic charge on the nuclei in the liquid medium. Fig. 9 presents the SEM particle morphology for ACS BT particles from water and from t-amyl alcohol, as examples, both showing generally a spherical shape. The OH⁻ content in the ACS BTs determined by FT-IR showed less OH⁻ in BTs from non-aqueous liquid than from the water medium as shown in Table 4.

The room temperature XRD patterns of BaTiO₃ formed in water medium at different stages are shown in Fig. 10. It clearly shows that crystalline BaTiO₃ was

Table 4. Semi-quantitative analysis of water content by FT-IR

Media	Toluene	n-butanol	Tertamyl alcohol	Water
Peak ratio	0.51	0.59	0.61	0.69

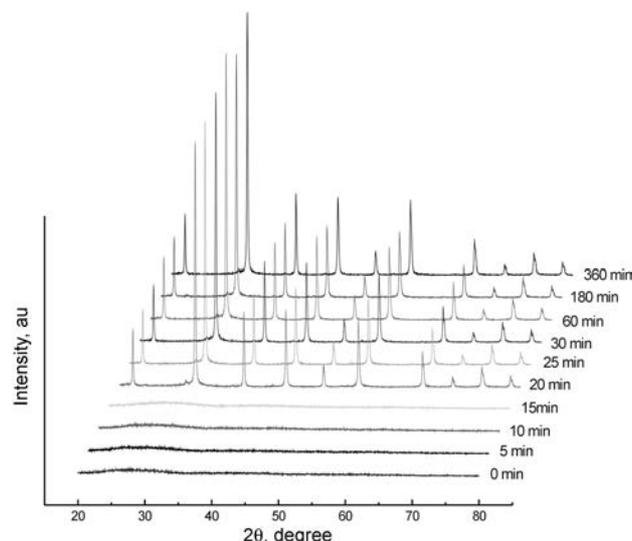


Fig. 10. XRD patterns of BaTiO₃ synthesized in water medium at different reaction time.

formed at 20 min after the start of the reaction and the crystallite size, determined by XRD line broadening, remained around 60 nm once the crystalline BaTiO₃ formed as shown in Table 2. Since there is big difference in terms of phase transformation from amorphous to nanocrystalline between the 15 min sample and the 20 min sample, the TEM study was mainly focused on these 2 transition points. Fig. 11a shows the bright field image of the 0 min sample. Irregularly-shaped agglomerates ranging from several hundred nanometers to several microns can be seen across the field. In the high resolution mode (Fig. 11b), no evidence of any crystallinity could be seen in the big lump of precursor, indicating that the 0 min sample, i.e., the precursor, consisted mainly of amorphous gel. This is in agreement with the XRD results in Fig. 10. TEM micrographs of the 5 min sample and the 10 min sample were similar to the 0 min sample in which no crystallites were found. However, the bright field image of the 15 min sample, as shown in Fig. 12a shows that the big amorphous gel was broken down into smaller pieces no bigger than one half micrometer. In the high-resolution mode (Fig. 12b), several tiny crystallites with dimensions of less than 10 nm were found in the amorphous gel, possibly from the diffusion of Ba ions into the gel and a Ba-Ti reaction [35]. However, since the size of nuclei is less than 10 nm, the overall RTXRD pattern of the 15 min sample still appeared amorphous (i.e., peak broadening effect leads to no peaks in the 15-min diffractogram in Fig. 10).

The bright field image of the 20 min sample was quite different from those previous samples. A large

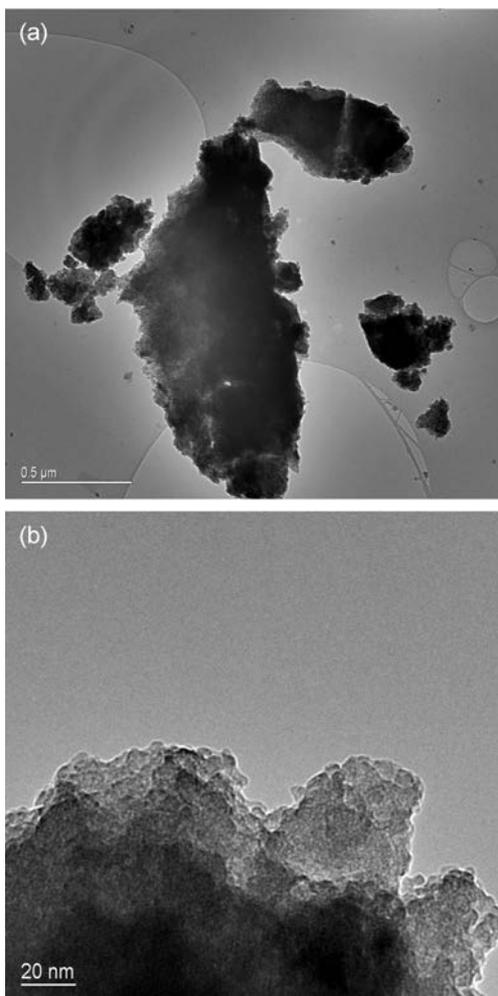


Fig. 11. TEM micrographs of 0 min sample, (a) bright field image; (b) high resolution mode of an edge of precursor gel.

number of well-dispersed spherical particles with dimensions in the range 60-100 nm were formed (Fig. not shown). The average size of these particles is agreeable with the DLS measurements (Table 2). The fringe spacings (2.3201 Å) in Fig. 12b are consistent with those that would be expected for cubic-phase BaTiO₃ ($d_{111}=2.3196$ Å), which is also in agreement with RTXRD results (Fig. 10). The particles seen from TEM bright field micrographs of the 30 min and the 360 min samples (Figs. not shown) were essentially the same as that of the 20 min sample.

Based on the microscopical observations, we propose the “in-situ transformation” mechanism for BaTiO₃ formation in the aqueous ACS process. The titanium-barium precursor formed amorphous gels after hydrolysis at high pH. As the temperature increased, tiny BaTiO₃ nuclei (<10 nm) were formed within the amorphous precursor gels in a short time (15 min) at relatively low temperature, e.g., ~75°C. Then the nuclei grew by combining to each other to form BaTiO₃ particles with dimensions of 60-120 nm. In the ACS refluxing conversion process as described in this paper,

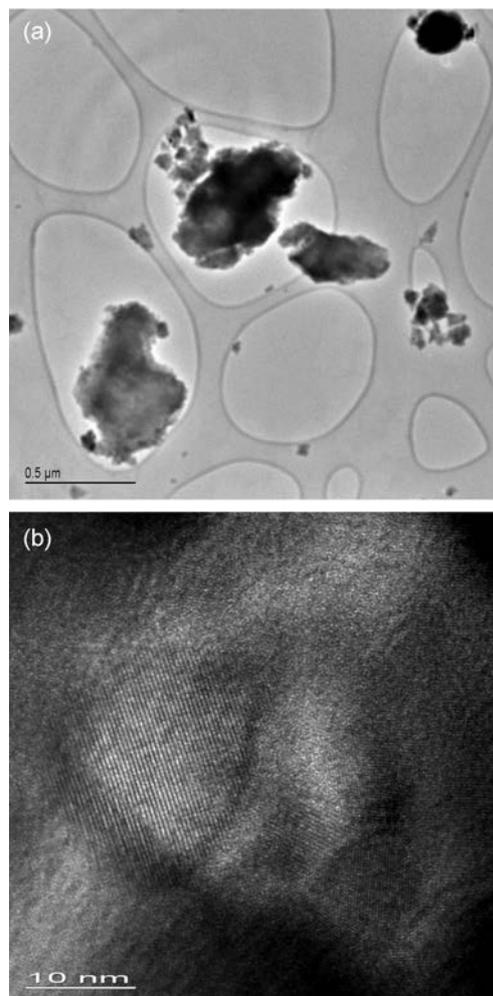


Fig. 12. TEM micrographs of 15 min sample, (a) bright field image; (b) high resolution mode showing the formation of small BaTiO₃ crystallites.

no evidence of a “dissolution-precipitation” mechanism was observed.

Conclusions

Results from EDTA titration of free Ba²⁺ ions leaching from BT provide the following conclusions:

- EDTA titration is an effective way to measure for Ba²⁺ ion leaching from BT in water.
- The extent and rate of Ba²⁺ ion leaching are significantly affected by solution pH; i.e., the higher leaching amount and the faster leaching rate occur at lower solution pH.
- Pre-heat treatment of BT powder in air enhances the Ba²⁺ ion leaching rate due to the formation of the soluble carbonate which has no passivating capability for Ba²⁺ ion leaching.
- The organic passivation agents were effective only at higher pH. This must be related to the morphology of the adsorbed organic passivation agents which is a function of the medium pH.

BT nanocrystals and redispersible particles can be

formed in toluene, n-butanol, tert-amyl alcohol and water under an ambient condition in solution. These nanocrystals were identified as metastable cubic phase BT by RTXRD and FT-Raman. BT powders prepared in non-aqueous media have a lower -OH content. The ACS refluxing method allows in situ sampling at ambient conditions. It was found that the formation of BaTiO₃ in water from the amorphous precursor is a rapid process. BT nuclei were formed at around 75°C, 15 min after the beginning of the ACS process. Individual BT particles with dimensions in the range of 60-120 nm were formed 5 min after the nucleation of nanocrystals. It is proposed on the basis of the microscopical observations that an in situ transformation mechanism, rather than a dissolution-precipitation mechanism, is dominant in the early stage of BT formation.

Acknowledgements

This work was sponsored in part by the Division of Materials Science, Office of Basic Energy Sciences of the U.S. Department of Energy at Oak Ridge National Laboratory under contract DE-AC05-00OR22725 and in part by the U.S. National Science Foundation under the grant no. DMR-9731769.

The authors would like to thank Dr. S. Costantino of Cabot Performance Materials for supplying BT-8 powder. Any opinions, findings and conclusions, or recommendations expressed here are those of the authors and do not necessarily reflect the views of the sponsors.

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