



Chemical Variations in Barium Titanate Powders and Dispersants

BURTRAND I. LEE

Department of Ceramic and Materials Engineering Clemson University, Clemson, SC 20634-0907

Submitted September 30, 1997; Revised April 14, 1998; Accepted October 20, 1998

Abstract. Commercial raw materials for multilayer ceramic capacitors—barium titanate (BT) and ammonium polyacrylate (APA) dispersant—were examined for lot-to-lot variations which cause poor reproducibility in BT slips and in capacitor chips. Two lots of BT supplied by a commercial source were different with respect to surface species examined by Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, electrokinetic sonic amplitude and total carbon analysis. It was found that there was more APA dispersant chemisorption on BT when the BT surface was more hydroxylated and less carbonated. For the dispersant, the two lots differed in pH and ammonium ion content. The amount of APA dispersant adsorbed on BT depended more on the ceramic powder surface species than on the chemical differences in APA lots.

The electrokinetic sonic amplitude (ESA) and zeta potentials of the two lots of as-received BT were small but positive. The BT lot with more surface hydroxyls exhibited slightly higher zeta potential values. The BT with more carbonate was more stable in terms of aging rate in water. Aging in water increased the positive zeta potential by increasing Ba^{2+} dissolution and adsorption. With the APA dispersant, the BT surface became less positive, but more stable and exhibited an isoelectric point of ~ 10.6 . It can be concluded that the dispersion of BT in the as-dispersed pH range is mainly by steric stabilization with little contribution from electrostatic charges.

Keywords: barium titanate, dispersant, variations, surface, infrared spectroscopy

1. Introduction

Barium titanate (BaTiO_3 : BT) possessing the tetragonal perovskite structure belongs among ferroelectric materials with interesting electrophysical properties including the high dielectric constant. BT-based dielectrics have dominated the multilayer ceramic capacitor (MLCC) industry since the 1950s, representing 80–90% of the business. [1,2]

BT is a relatively stable refractory compound that can be synthesized easily by reacting BaCO_3 with TiO_2 . Two of the more important BT performance parameters are chemical purity and particle size. Improvements in the chemical purity of starting materials have been a major objective within the MLCC industry. For BT material, the ability to increase the dielectric constant is limited. Hence, reduction in dielectric layer thickness has received attention for high performance MLCCs. These thinner dielectric layers have not only further increased

demands on raw materials control, but also have put new demands on MLCC processing. BT, as a member of the perovskite family, is thermodynamically unstable and reactive in an aqueous environment as well as moisture and carbon dioxide in air. This can gradually change the surface species and stoichiometry which obviously will affect the surface chemistry of the powders, and thus the reproducibility and performance of MLCCs.

In BT tape casting, fine BT powder is dispersed in a liquid medium containing various ingredients. They include stabilizers, polymer binders, wetting agents and many other ingredients to satisfy the performance requirements of MLCCs and various processing demands to obtain a castable BT suspension called “slip”. Any variations in any one of these ingredients can affect the slip properties, and hence, the castability and reproducibility which essentially affect the performance and quality of capacitor chip products.

Reliability problem of BT capacitors due to aging of BT materials was noticed years ago by many investigators [3–7]. However, no one has addressed the variations in raw materials at the slip level of capacitor fabrication. Although some of them observed variability, and a degradation of electrical [8] and physical properties [9,10] with time in the capacitors fabricated from commercial materials, they did not point out the possible causes of the variations in the raw materials.

Dissolution of BT in high dielectric constant liquids including water have been studied by Adair et al. [11–13]. Harard et al. [9] investigated five different commercial BT powders and found that all of them were contaminated with significant amount of carbonates, resulting in poor green density of the BT casts. Hung and Riman [14] estimated, using XPS, large amounts of Ba rich impurities present in hydrothermally prepared BT surface.

Due to the complex nature of BT slips, the MLCC industry is currently experiencing reproducibility problems in the slips, tapes and MLCC chips. A better understanding of the physicochemical nature and the causes of the problem in the commercial raw materials is much desired. This paper reports the existence and the nature of variations in commercially obtained raw materials of BT powders and dispersants. The information in this paper provides the basis for further studies on how to deal with practical short-term, as well as long-term, solutions to the problems associated with handling ferro- and dielectric powders.

2. Experimental

2.1. Materials

Two lots of a commercial BT powder (BT1 and BT2) were obtained from Transelco Division, Ferro Corp., Penn Yan, NY. According to the materials specification data (M-Spec) the powders have 1.1–1.3 μm particle diameter, 1.8–2.5 m^2/g surface area and Ba/Ti ratio of 0.990–0.999.

For aqueous processing of BT, polyacrylate dispersants are widely used. Two different lots of ammonium polyacrylate (APA) were obtained from Henkel Corp., Ambler, PA.

2.2. Instrumental

The surfaces of the as-received barium titanate powders from 2 different lots were examined using Fourier-transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), total carbon analysis, and electrokinetic sonic amplitude (ESA). These methods were used to detect any impurities on the powder surface and the degree of surface hydroxylation, which will affect the electrostatic charging of the particles, wettability of the dispersant, pH of the suspension, and zeta potential of the particles.

FT-IR spectra were obtained using a Bruker FT-IR Model IFS28 at 500 scans and a diffuse reflectance stage, specular reflectance stage, or KBr pellets, depending on the sample phase, with a mercury-cadmium-telluride detector. An FT-IR technique referred to as diffuse reflectance infrared fourier transform (DRIFT) was carried out by placing 237 mg of sample powder on the sample cup of the DRIFT stage. For liquid samples, BaF_2 plates were used to hold the samples. Semiquantitative comparisons of the functional groups were made by taking ratios of the corresponding peak heights using the baseline method. The amounts of total carbon were determined by using a Leco Carbon Analyzer. XPS was done by using an X-ray Photoelectron Spectrometer Surface Science Model SSX 100 which yields 4 eV resolution with 10 scans. The electron flood gun was set at 8.5 eV. Semiquantitative analysis for the Ba/Ti atomic ratio were carried out by integrating the areas under the respective peaks. ESA was done by using ESA-8000 Electrokinetic Analyzer at Matec Applied Science, Hopkinton, MA.

2.3. Procedure

Dissolution of BT in a measured amount of water (50 wt% solids) was examined in the presence (2.2 wt% of BT) and absence of the APA dispersant and this was correlated with the pH measurements. The samples were prepared by aging a known weight of as-received BT in water at 55 °C in sealed polypropylene bottles for 49 h for the BTs and 64 h for the BT+APA followed by centrifuging. The supernatant was immediately acidified with 10–20 drops of conc. nitric acid to prevent any metal hydroxide precipitation. The dissolved metals in the supernatant were quantitatively determined by using a

Perkin-Elmer Atomic Absorption Spectrometer Model 5000.

The adsorption behavior of the dispersant APA on BT was examined by dispersing 20 g of BT in 50 ml of water with 0.4 g of APA in an oven at 55 °C for 64 h. The slurries of BT after aging were centrifuged, washed, and dried. The dried powders were placed in ceramic crucibles in a Leco Carbon Analyzer to determine organic content.

An ESA-8000 apparatus was used to examine four samples of BT powders: 2 lots of as-received BT; BT aged in 2.1 wt% APA solution for 48 h at 50 °C, followed by air drying; and BT aged in water for 48 h at 50 °C without APA, followed by vacuum filtering and washing with deionized water 2x. The sample suspensions for ESA were prepared by dispersing 20 g of the BT powders in 250 ml of deionized water without supporting electrolytes. Some suspensions were aged for 0, 24, and 53 h before the ESA measurements. Each sample was titrated with 1 N hydrochloric acid or potassium hydroxide to vary the pH of the medium.

3. Results and Discussion

3.1. BT Powders

FT-IR spectra for the 2 lots of BT shown in Fig. 1 reveal that there are quantitative differences between the 2 BTs. The possible band assignments in the different wavenumber (ν) regions were carried out using the spectral data available in the literature [15–18]. When compared with a reference spectrum of BT

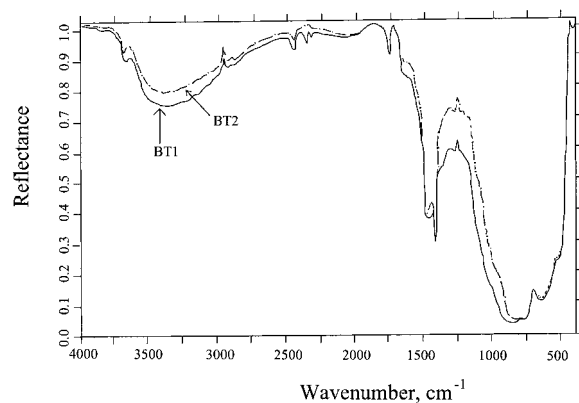


Fig. 1. DRIFT spectra of 2 lots of as-received Transelco BT lot no. 1 and 2.

from the Sadtler collections [17], the spectra identified some impurities on the BTs. The survey spectra of BT1 and BT2 were superimposed with respect to the BT peak at 750 – 470 cm^{-1} . It appeared that there are more –OHs and carbonates on BT1 based on the direct comparison of the band intensities. Since the band intensity can fluctuate by the instrument settings, sample amount, noises, etc., band intensity ratios were taken to estimate the semiquantitative trends of the functional groups present in the BT samples. The band intensity (I_ν) ratios from enlarged spectra and the functional group assigned to the bands using the baseline method are given in Table 1. It basically shows that BT1 is covered more with carbonate and BT2 with –OH. This is understandable since BT1 is older and had been exposed to air longer than BT2. The –OH on BT1 had more time to be converted to –CO₃ by the reaction with atmospheric CO₂.

The amount of total carbon in the BTs determined by the Leco Carbon Analyzer showed 482 ppm in BT1 and 458 ppm in BT2 as given in Table 2. The FT-IR results in Table 1 agree with the total carbon content results in showing that there is slightly more (~5–10%) carbonate on BT1. The DRIFT peak ratios also indicate that BT2 is slightly more hydroxylated than BT1. If this is the case, the surface covered with more OH should give stronger electrostatic repulsive forces via higher surface charge density because of the greater availability of the charging sites. This can result in more adsorption of an oppositely charged ionic dispersant on BT2. Indeed this was observed and the results are also listed in Table 2. The more OH on the BT2 surface, even after considering ~20% larger

Table 1. FT-IR peak ratios from BT spectra

Peaks	Peak ratios	
	BT1	BT2
Lattice OH/hydrated OH		
I_{2885}/I_{3385}	0.21	0.23
Hydrated OH/BT		
I_{3385}/I_{750}	0.83	1.0
BC/BaO		
I_{1750}/I_{1670}	1.9	1.0
BC/BT		
I_{2452}/I_{2364}	0.98	0.94
I_{2451}/I_{615}	4.1	3.1
I_{2451}/I_{750}	2.2	2.0

Table 2. Total carbon on as-received BT and APA adsorbed BT

Sample	Surface area, m ² /g	Total carbon, ppm	Carbon from APA, ppm
BT1	1.9	482 ± 0.8%	
BT2	2.4	458 ± 1.3%	
BT2/APA1		1967 ± 1.5%	1509 ± 1.5%
BT2/APA2		1926 ± 0.5%	1468 ± 1.8%
BT1/APA2		1346 ± 1.8%	864 ± 1.5%

specific surface area of BT2, led to ~30% greater adsorption of the dispersant APA on BT2 than on BT1.

The XPS survey spectra showed peaks for Ba, oxygen, and carbon at 792 and 776, 527, and 283 eV binding energy, respectively. Both lots showed diminishing carbon peaks by argon ion sputtering which removed carbonaceous species. The Ba/Ti atomic ratios from the XPS given in Table 3 which show rather large Ba/Ti atomic ratios, indicating excess barium on the surface of 10–50 Å depth. The trend of higher Ba/Ti ratios for BT2 than for BT1 agrees with the Ba/Ti ratios in M-Spec. However, we see much larger Ba excess from the XPS analysis. The difference is that XPS probes only the surface of 10–50 Å layer, while the M-spec reports the bulk composition. The M-Spec's acetic acid soluble Ba, total carbon (Table 2), and FT-IR data all suggest that there is more carbonate on BT1 than on BT2. Then the greater excess of Ba on BT2 shown by XPS must be from barium-rich phases such as Ba₂TiO₄, barium oxides and hydroxides in addition to carbonates.

The larger deviations from the stoichiometric Ba/Ti ratio of 1.0 in the XPS data after sputtering were unexpected. Much longer sputtering time and a true depth profile would be helpful to explain this fact better. Unfortunately, there is no reliable depth profile method currently available for powder samples. A high resolution XPS study to distinguish the different chemical environment of Ba²⁺, i.e., how much of the surface Ba²⁺ is from –OH, –CO₃ or Ba₂TiO₄, would be desirable.

Table 3. Barium to titanium atomic ratio probed by XPS for 2 different lots of BT

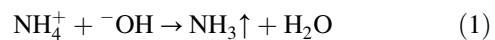
BT lot	Ba/Ti ratio	
	Before	After sputtering
1	1.50	1.77
2	1.77	1.93

Another possibility is the preferential sputtering of Ti to Ba. Balaz et al. [19], in their study of BaCO₃ + TiO₂ + PbO mechanical mixture, observed at least 2 chemically different Ba, O and C in their XPS spectra. Argon ion sputtering caused decomposition of CO₃²⁻ species and reduction of titanium oxide. This would then explain the high Ba/Ti ratios in this study of BT powders.

Aging behavior of BT in water directly affects the surface compositions and stability of the particles in a slurry. One of the more obvious causes of the aging is dissolution. The basic nature of barium oxide tends to cause dissolution in the acidic medium leaving a Ti-rich layer. In air, Ba–O will react with the acidic CO₂/H₂O, yielding Ba–CO₃. This will not only change the composition of the material but also change such properties as the surface charge of the BT, pH of the medium, solubility and adsorption of additives, etc.

3.2. APA Dispersant

The dispersibility of BT, in the presence of ammonium polyacrylate (APA), comes from the action of the polyacrylate anions. At basic pHs and/or at elevated temperatures, the cation NH₄⁺ escapes as NH₃ gas as shown in Eq. (1).



Some ammonia would be lost during mixing and particularly during milling with APA when the slurry temperature rises. When this occurs, the pH of the system must be lowered. In Fig. 2, the pH of APA is decreased by stirring in an open atmosphere at 40 °C. The pH dropped from 7.6 to 7.4 in 44 h. The pH values of APA from lots no. 1 and 2 after treating under different conditions and measuring at different times are given in Table 4. This table clearly shows the more acidic nature of APA lot no. 1 and the loss of ammonia by open stirring.

The band ratios from FT-IR spectra for APA

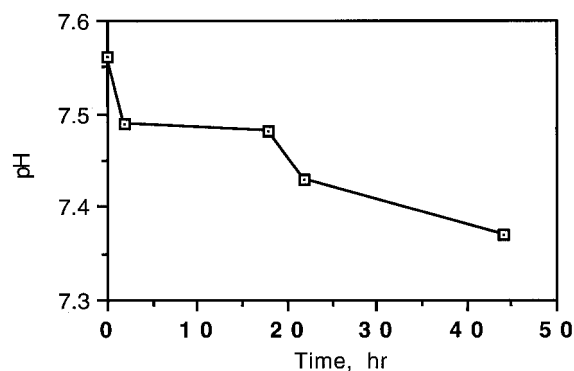


Fig. 2. pH changes of APA with time under open and warm stirring.

Table 4. pH values of APA under different conditions

Treatment condition	pH	
	APA 1	APA 2
Fresh	7.60	7.76
Open/stirring 44 h		before after 7.74 → 7.58

samples placed between IR transmitting BaF₂ plates showed quantitative differences in the regions of 3380 – 2680 cm⁻¹ and 1750 – 500 cm⁻¹. Using the enlarged peaks from the selected regions of wave-numbers, the band ratios were calculated. The values of the band ratios given in Table 5 showed that APA lot no. 1 contained the least NH functional groups, and lot no. 2 and lot no. 2 with added NH₄OH, the most. The FT-IR method adopted here would be valid only for total NH in terms of NH₄⁺ ion since the samples were prepared by spreading a drop of APA between two barium fluoride plates. In any case, the trend agreed with the pH values and the resulting dispersibility of APA lot no. 1, yielding slips with poor reproducibility. The results must be related to the lower content of ammonium ion in APA1.

The lower NH content in APA affecting the dispersibility of BT may be explained in two ways. One is that the less NH in the form of NH₃ would exhibit lower pH of the slurry, leading to lower electrostatic contributions to the dispersibility depending on the isoelectric point of the BT. As shown in Fig. 3, the lower pH also affects the conformation of the polyacrylate adsorbate. Polyacrylic acid (HPA) is a weak acid and behaves like a multibasic saturated acid. Potentiometric

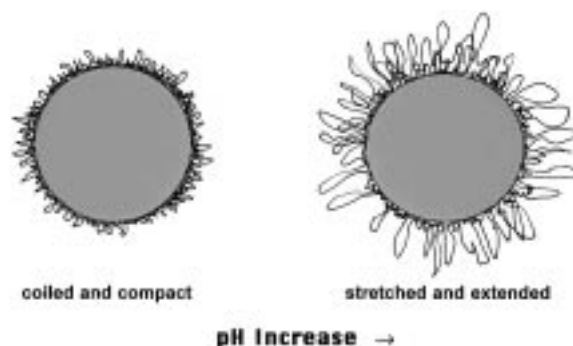
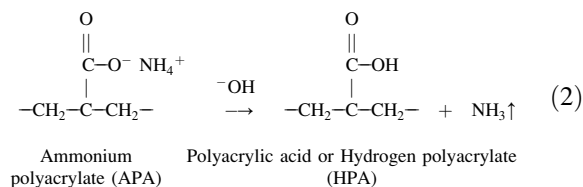


Fig. 3. pH dependent conformation of polyacrylate molecules adsorbed on BT.

titration curves by Mathiesen and McLaren [20] revealed 2 different molecular conformations. At a lower pH, the adsorbate molecules are more coiled and compact [21–23]. In this case, simple additions of NH₄OH to the slurry or to the APA should help restoring the reduced dispersibility. The other case adversely affecting the dispersibility by the loss of ammonium ions via NH₃ may be shown by the Eq. (2).



As the equilibrium shifts to the right by the loss of NH₃, more HPA is formed at the expense of APA. The solubility and the charge of polyacrylate anion would then be reduced in addition to the coiled conformation on BT. Since this violates two of the conditions for effective dispersion via steric hindrance, dispersibility must decrease. This shift of the equilibrium to the right can be monitored by pH, conductivity or ion concentration. pH or conductivity decrease may indicate the formation of more HPA and reduction in APA. This was indeed observed in Al₂O₃ [21] and TiO₂ [24] and the stability of the suspensions were highly pH-dependent for HPA dispersant.

3.3. Adsorption Isotherms, pH Changes and Dissolution

The amount of APA adsorbed on BT was determined by measuring the total carbon content and subtracting the amount of carbon on the as-received BTs. From

Table 5. FT-IR peak ratios from different APAs

I_{ν_1}/I_{ν_2}	Functional group	Peak ratios			
		APA1	APA2 new	APA2 boiled	APA2 boiled + NH ₄ OH
3220/684	NH ₄ OH/CH ₂	3.3	9.1	7.6	8.4
1640/684	NH/CH ₂	0.33	1.1	0.7	1.25
3246/723	NH/CH ₂	3.1	8.9	7.4	8.2

this estimate given in Table 2, it can be calculated that 1509 ppm carbon in BT1/APA1 corresponds to 1509 mg/kg or 0.15 wt% adsorption. Since the APA addition was at 2.2 wt%, this gives ~7% adsorption with respect to BT or ~18% with respect to water, implying that ~80% APA is unadsorbed.

The greatest adsorption of APA1 for BT2 and the least on BT1 by APA2 may be explained by an acid-base interaction of BT and APA on the surface. It has been shown in the previous sections discussing FT-IR results that BT2 is covered more with Ba–OH than Ba–CO₃ while BT1 is covered with more –CO₃ than –OH. In this case, the surface of BT2 would be more basic than BT1, while APA1 is more acidic and covalent than APA2 shown by FT-IR and the actual pH measurements (Table 4). Hence the more adsorptive interaction is favored between APA1 and BT2.

pHs were measured for BT powders in water with and without APA as a function of time. The pH of a 50 wt% BT suspension in water read 11.82 after the suspension was aged at 55 °C for 49 h in a sealed polypropylene bottle. Within this time period at the temperature, significant Ba dissolution (1.3 g Ba/kg BT or ~10⁻²M Ba²⁺) took place as shown in Table 6. In the presence of ~2 wt% APA the pH dropped to 9.70, indicative of a reduced dissolution of Ba as hydroxide. The adsorbed APA reduced the dissolution of Ba by a factor of ~2.6x and Ti by more than 4x. APA is shown to be effective in passivating the BT surface, though incompletely. The difference in the

Table 6. Dissolution of BT in water at 55 °C for 40h determined by atomic absorption spectrophotometry method

BT	Ba	Ti
	in ppm	
BT2	1330	4.7
BT2/APA2	515	< 1
BT1/APA2	520	< 1

dissolution of Ba and Ti between BT lots 1 and 2 in the presence of APA was very small and is perhaps insignificant. As shown in Table 2, there was more APA adsorption on BT2 than on BT1. This should help reducing the dissolution in BT2. Alternatively, the little larger amount of carbonate in BT1 must have counteracted the dissolution of Ba and Ti in BT1.

3.4. Electrokinetic Sonic Amplitude

The electrokinetic sonic amplitude (ESA) technique can measure particle dynamic mobility of BT particles dispersed in liquid media. ESA of BT powders dispersed in a liquid medium depends on the surface characteristics of BT particles including particle size. Unlike conventional electrophoretic techniques, ESA can examine concentrated slurries up to ~40 vol.% in both aqueous and nonaqueous media. In ESA, an alternating electric field is applied on a particle suspension by electrodes. Further details on ESA can be found in [25–27].

As the charged particles move backward and forward, sound wave emanates from the electrodes. The amplitude of the sonic wave, ESA, is directly proportional to the particle mobility and the dynamic mobility is related to zeta potential in the following manner,

$$\mu_d = \frac{2\varepsilon\zeta}{3\eta}G \quad (3)$$

where, G = complex function relating to electric field around particles and particle inertia.

ε = dielectric constant of medium

η = viscosity of medium

ζ = zeta potential

ζ is calculated from the measured ESA. It is well known that ESA and thus ζ is a function of particle size [28] for the size $\geq 1 \mu\text{m}$ affecting the inertia term in Eq. (3). The background electrolyte or the ionic strength of the medium is also known to affect the

ESA, and hence, ζ by affecting the double layer thickness [26,29,30]. The effect of background electrolyte is pronounced for ion concentrations > 0.01 M [29,31]. Several researchers, however, did not consider the effect of background electrolyte on the ESA and ζ in their study of CaCO_3 , BT, and oxide phosphors [32–35].

In this study, the absolute ζ values, for not maintaining the ionic strength of the medium constant, may not be accurate. Therefore, the ζ values of BT in water during aging must be only interpreted in relative terms, i.e., the difference between two lots of barium titanate powders rather than determining the values or comparing ESAs in absolute sense. In this case, the effect of the background electrolyte was assumed to be indistinguishable, since the ionic strength of the medium due to BT dissolution is rather high (as high as 10^{-2} M). The relative comparisons were considered to be more meaningful from the real processing situations of no added electrolytes. Moreover, the use of supporting electrolyte at $\sim 10^{-3}$ M would have been impractical when the ionic strength of the system is already higher than that by the lattice dissolution, i.e., the conductivity of 300–800 $\mu\text{S}/\text{cm}$ as shown in Table 7.

The results of the initial ESA values (at the first pH point) along with the corresponding ζ in mV, pH, conductivity in siemens per cm and isoelectric points (IEP) are given in Table 7 for the two lots of BT

treated differently. Table 7 along with Figs. 4 and 5 show that the ESA and zeta potentials of as-received BTs are very small but positive. The positive values must be from the dissolved and readsorbed Ba^{2+} ions which also caused the high pH of 10.7. This is similar to the results of Huang et al. [32] who observed positive ζ by the readsorption of dissolved Ca^{2+} in a calcium carbonate slurry. They, too, assumed constant particle size during the course of titration for the ESA analysis. The ESAs plotted as a function of pH for as-received BT1 and BT2 after aging for different lengths of time reveal a faster aging rate of BT2 than BT1 by exhibiting no further changes in ESA after 26 h of aging for BT2. Aging in water at room temperature increased the positive $\zeta \sim 3$ x in 25 h by the increased dissolution of Ba^{2+} which is shown by the increase in the conductivity and pH. This trend was observed in both BTs although the ζ , pH and conductivity are a little higher for BT2. The little higher ζ , pH and conductivity values for BT2 are consistent with the FT-IR results on a greater amount of Ba-OH and APA adsorption on BT2. The differences between BT lots 1 and 2 presented and discussed in the previous sections (e.g., BT1 is more passivated by carbonates than BT2, and hence less lattice dissolution occurs) are in good agreement with the ESA results.

Both as-received BTs showed no IEP within the pH range of ~ 3 – ~ 11 . Similar results, quantitatively and qualitatively, were obtained by Chen et al. [34] They

Table 7. ESA, zeta potential and conductivity of barium titanates in water

Sample	Aging t. h	ESA mPa•M/V	ζ mV	pH	Conducti. $\mu\text{S}/\text{cm}$	IEP
BT1	0	0.122	2.1	10.7	283	> 12
	25	0.327	5.7	11.1	523	none
	53	0.396	6.5	11.1	614	none
BT2	0	0.180	3.1	10.8	339	> 12
	26	0.509	8.7	11.3	735	none
	54	0.514	8.8	11.2	780	none
BT2 aged, filtered washed&dried	0	-0.478	-8.2	8.5	70	< 3
	29	-0.173	-3.1	8.4	101	< 3
BT2/APA2 dried	0	0.032	0.6	9.2	56	10.5–11
	29	0.038	0.7	9.2	62	10.7–10.9
	0					10.4
	29					10.6

also did not use a background electrolyte nor did they consider the potential particle size variations in their acoustophoretic characterization of BT.

Titration of the suspension using 1 N HCl, the ESA increased somewhat or became nearly constant down to pH \sim 7. Below pH 7, the ESA decreased until it reached a minimum at pH \sim 4.5, below which the ESA shot up at pH \sim 3. This trend is common to both BT lots. It seems that at pH \sim 7, the protective carbonate layer on BT begins to break down, exposing the Ti-rich layer. However, the decreasing trend is reversed as the pH is changed below \sim 4.7, indicating accelerated Ba dissolution as shown also by the high conductivity of \sim 300–800 μ S/cm for as received (or unprotected) BTs in 50 h.

Specific adsorption of Ba^{2+} on BT and the compression of double layer compression by the

electrolyte must apply to the slurries in this study. The high conductivity of the slurries as shown in Table 7 affected the ESA values in two ways: one is the compression of the double layer thickness and the other is affecting the zeta potential in an opposite way, by increasing the potential by specific adsorption of the cations, barium in this case. However, the precise effect of Ba^{2+} ions in a BT slurry on the two opposing factors and on the background electrolyte needs to be studied further under more controlled conditions.

When BT2 powder had been pretreated by aging, filtering, washing and drying, the ESA and ζ indicate surface charge reversal, i.e., from small positive to small negative as shown in Table 7 and Fig. 6. This is an indication of removal of the readsorbed cation Ba^{2+} by washing. The washing left a Ti-rich BT surface which explains the lower pH and conductivity

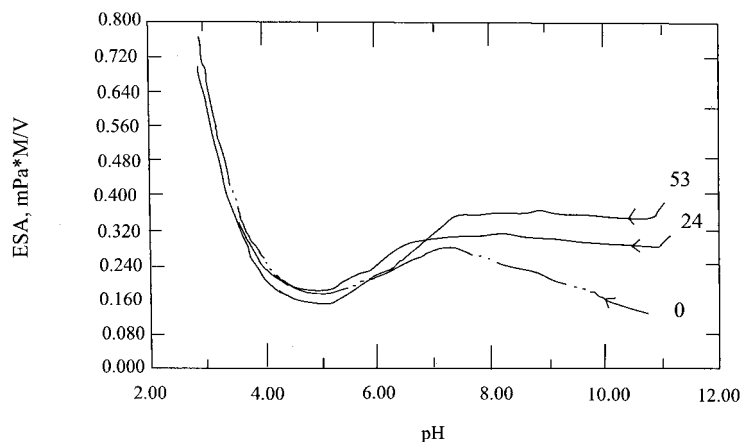


Fig. 4. Electrokinetic sonic amplitude vs. pH plots for BT1 after aging for different length of times.

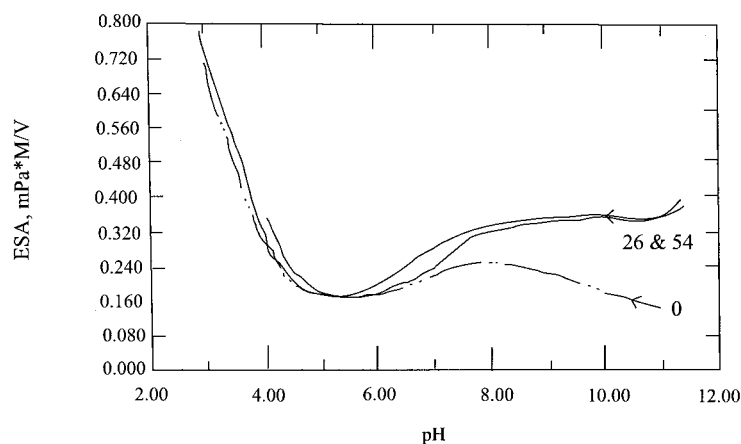


Fig. 5. Electrokinetic sonic amplitude vs. pH plots for BT2 after aging for different length of times.

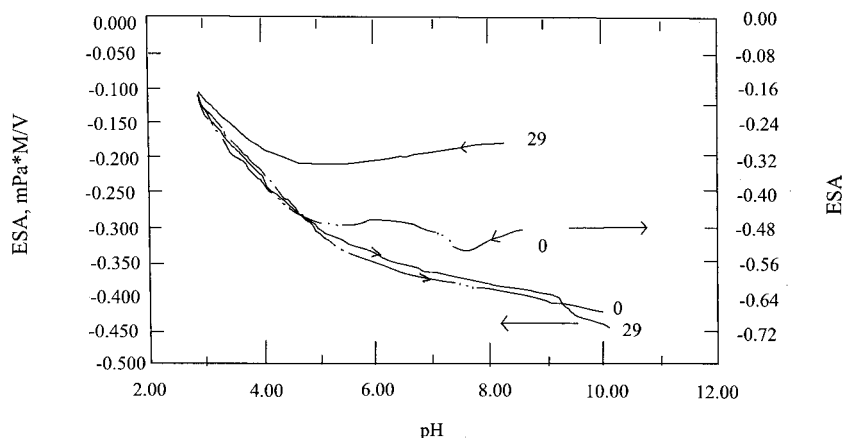


Fig. 6. Electrokinetic sonic amplitude vs. pH plots for BT2 of pre-aged in water, washed, and dried before the ESA measurements after 0 and 29 h aging in water.

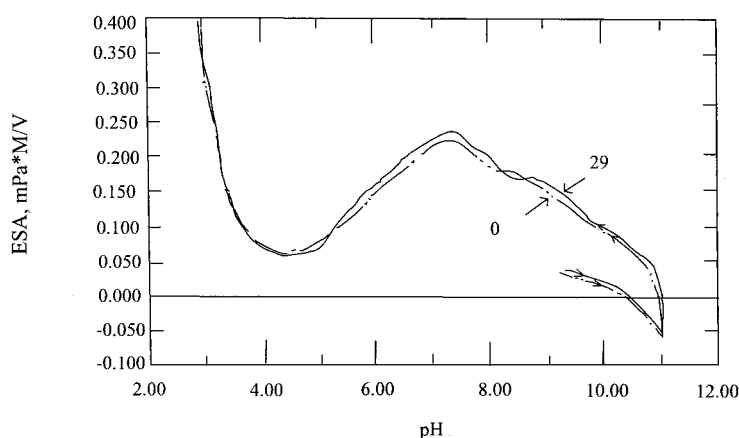


Fig. 7. Electrokinetic sonic amplitude vs. pH plots for BT2 pre-aged in APA/water followed by direct drying in air before the ESA aging experiment.

values. However, given that the IEP of TiO_2 is ~ 6 , the observed IEP below 3 is anomalously low. Washing Ba^{2+} ions from the surface of the BT made the surface very acidic. On the other hand, the low IEP is similar to that of Chen et al. [34] for a HPA coated BT. The excess polyacrylate anions, in the work of Chen et al. may have chelated the dissolved Ba^{2+} ions in the slurry, exhibiting the effect of removal of Ba^{2+} . With time in water the surface became less negative, indicating the resumption of Ba^{2+} dissolution, which is supported by the small increase in conductivity and by the enlarged hysteresis.

BT2 adsorbed with APA exhibited a very low positive initial ζ with pH of 9.2. Aging it for 29 h had minimal effect, as shown in Table 7 and Fig. 7. This is

consistent with the results previously discussed in the section for BT dissolution. When the suspension was titrated toward acidic pH, the positive ESA increased, reaching the maximum at $\text{pH} \sim 7$, followed by decreasing to a minimum at $\text{pH} \sim 4.3$. Then the ESA shot up at pH below 4. Aging the powder for 29 h made the ESA slightly more positive. These plots in Fig. 7 show that small positive zeta potential of ~ 2 mV can be realized at $\text{pH} \sim 9.5$. When the slurry was titrated with KOH, the IEP values was shown to be 10.4–10.7, with higher values for aging for 29 h in water.

APA was effective in reducing the dissolution of BT by adsorbing on the BT surface. The small ζ of as-received BT was further decreased to near zero by

APA adsorption. This means that the pH of BT slips being at or near the IEP, their stability is largely dependent on the adsorbed polymer APA at the processing pH. This demonstrates the increased importance of the role of dispersant in BT dispersion in an aqueous medium. The small positive charge of the as-received BTs by the readsorbed barium ions decreased to even smaller values by the adsorption of anionic dispersant. The dissolved Ba^{2+} ions, indicated by the high conductivity and atomic absorption results in Table 6, further weakened the electrostatic contribution to the stability of the system by compressing the double layer [36]. Thus, the dispersion stability of BT must rely on steric factor by the adsorbed polymeric chains.

The range of IEP ~ 10.5 – 10.9 indicates that there are active surface chemical reactions even within the small pH range during the titration. The observed IEP values in this work differ significantly from that one observed by Chen et al. [34]. Their IEP of BT adsorbed with HPA was ~ 3 . It appears that the BT suspension they used had HPA in a great excess (in the range of 2 wt%) in the suspension which caused multilayer adsorption as the pH was decreased by HCl solution. In this case the surface of BT must have behaved like HPA. To have appreciable electrostatic repulsive interactions between BT particles for a desired slip, one needs to keep the pH away from the IEP of ~ 10.6 . Practically, however, this is difficult because the initial pH is already so high as to change the pH toward the basic direction away from the IEP. Adjusting pH toward the acidic direction is undesirable for many other reasons such as enhanced BT dissolution, corrosion in processing equipment, etc.

4. Summary and Conclusions

The surface chemistry of BT in water is complex. The examination of two lots of commercial BT showed clear differences in surface properties which can affect dispersion stability and reproducibility of MLCC chips. The degree of carbonation of BT is inversely related to the degree of Ba^{2+} dissolution; i.e., the higher the degree of carbonation, the lower the degree of Ba dissolution. The converse is true for higher zeta potential values, adsorption isotherms of dispersant and the equilibrium kinetics of BT in aqueous media. XPS results suggest that the composition of the BT surface is nonstoichiometric. The zeta

potential of BT may vary not only by the pH but also by the barium ion concentration (or any other ions) and other adsorbed species. Thus, at a given pH, the BT surface can be either positive or negative. Further studies will be required to determine the effect of the surface carbonates and the dissolved Ba^{2+} on MLCC performance.

Some of NH_4^+ cations in APA were lost as NH_3 during processing. This affected pH reduction and dispersion stability. The anionic nature of APA dispersant must be considered for adsorption on BT and interaction with other constituents in the system. The loss of NH_4^+ at the pH of the BT slurry and temperature of the tape casting process is significant. When this occurs, two consequences are of importance. One is that the pH of the system is reduced. The other is the conformation of the adsorbed polyacrylate anions and the dependence of the APA adsorption isotherms on pH. Since pH is one of two mechanisms in determining the effectiveness of a dispersion, any drift in pH of the system would affect the reproducibility. However, the ESA results showed that the electrostatic charge contribution is very small in a BT/APA slurry. Electrostatic contribution to the dispersion may be increased by lowering the slip pH. However, BT dissolution becomes more pronounced, and APA anions will revert to polyacrylic acid which has a lower solubility and adsorbs in a compact and coiled configuration as shown in Fig. 3 and in Eq. (2). This makes the steric stabilization mechanism, which has been shown to be the predominant mechanism in BT slurries, less effective in this case. Thus, keeping the pH high is preferred for stable BT slips.

Acknowledgments

Financial and technical support for this study was provided by Kemet Electronics Corp. The electrokinetic measurements carried out by Mr. Russell Mann of Matec Applied Science are gratefully acknowledged.

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