

# Surface modification of BaTiO<sub>3</sub> with yttrium, and dissolution and adsorption/precipitation behaviors of BaTiO<sub>3</sub>

Seung-Mi Lee · Sangkyu Lee · Chae-Woong Cho ·  
Ungyu Paik · Dae-Hwan Kim · Eun-Sang Na ·  
Jea-Gun Park

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**Abstract** An attempt was made to retard the dissolution of Ba ions from BaTiO<sub>3</sub> by coating Y compounds on the BaTiO<sub>3</sub> particle surface. A hysteresis in the electrokinetic behavior of as-received BaTiO<sub>3</sub> occurred during sequential acid and base titrations, while there was no hysteresis in the Y-coated BaTiO<sub>3</sub>. In the bare BaTiO<sub>3</sub>, dissolved Ba ions are adsorbed and/or precipitated onto the surface during sequent base titration to yield a more positively charged Ba-rich phase on top of the Ba-depleted lattice. On the contrary, the dynamic mobility of Y-coated BaTiO<sub>3</sub> during base titration closely followed the corresponding acid titration, providing that the starting surface of Y-coated BaTiO<sub>3</sub> and the surface after acid-base treatment was the same. It is suggested that Y compounds on the BaTiO<sub>3</sub> particles retard the dissolution of Ba ions from BaTiO<sub>3</sub>.

**Keywords** Barium titanate · Yttrium coated BaTiO<sub>3</sub> ·  
Dissolution · Passivation

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S.-M. Lee · S. Lee · C.-W. Cho · U. Paik (✉)  
Division of Advanced Materials Science Engineering, Hanyang  
University, Seoul 133-791, Korea  
e-mail: upaik@hanyang.ac.kr

D.-H. Kim · E.-S. Na  
Samsung Electro-Mechanics Co. Ltd., Suwon 442-743, Korea

J.-G. Park  
Nano-SOI Process Laboratory, Hanyang University, Seoul  
133-791, Korea

## 1 Introduction

Barium titanate (BaTiO<sub>3</sub>) has been extensively used in multilayer ceramic capacitors (MLCCs) due to its superior dielectric properties [1]. The dielectric layers in MLCCs are generally fabricated by tape-casting or lip-coating. Production of green tape with a high packing density and uniform particle distribution is dependent on controlling the stability and chemistry of the ceramic suspension. To obtain a suspension suitable for the casting, organic solvents have traditionally been used as the suspending medium. Although the non-aqueous system has some advantages, including a faster drying rate, lower capillary forces, and typically a higher green strength of tapes [2], there has been a recent push towards aqueous-based tape-casting for cost-related and environmental benefits. However, a critical shortcoming associated with aqueous-based systems is the incongruent dissolution of BaTiO<sub>3</sub> and the resulting accumulation of Ba<sup>2+</sup> in solution [3–7]. As recent investigations [8, 9] have shown, the dispersion stability of colloidal BaTiO<sub>3</sub> is closely tied to changes in the surface chemistry that result from Ba<sup>2+</sup> leaching. Dispersion stability has a critical impact on particle packing [10], which in turn influences the microstructure and electrical properties of the sintered dielectric layer [11]. In addition, the dielectric and microstructural properties of BaTiO<sub>3</sub> are very sensitive to stoichiometry, and small deviations may cause a significant deterioration [7, 12, 13] or enhancement of the dielectric response [13]. In our previous study [14], the surface composition of BaTiO<sub>3</sub> powders was varied during wet processing by the dissolution and precipitation of Ba<sup>2+</sup>, which has an influence on the microstructure and electrical properties. Understanding passivation at the BaTiO<sub>3</sub>—aqueous solution interface is therefore essential for establishing predictable and reliable aqueous-based tape casting. An attempt [15] was also made to restrain the

dissolution of  $\text{Ba}^{2+}$  from  $\text{BaTiO}_3$  surface by utilizing dispersant and binder.

An improvement in the lifetime of MLCCs is another critical factor that should be considered in MLCC fabrication. Yttrium has been considered the most effective element for an improvement in the reliability of MLCCs [16].  $\text{BaTiO}_3$  and  $\text{Y}_2\text{O}_3$  are generally mixed by mechanical milling; homogeneous distribution of  $\text{Y}_2\text{O}_3$  is difficult to achieve because of the segregation of  $\text{Y}_2\text{O}_3$  [16]. In this study, the  $\text{BaTiO}_3$  particle surface was modified with Y compounds to control the dissolution behavior of the Ba ion and obtain a homogeneous distribution of yttrium. The electrokinetic behavior of Y-coated  $\text{BaTiO}_3$  particles and the dissolution behaviors of Ba and Y ions were measured to evaluate the coating effect on the dynamic mobility and surface chemistry of the core-shell particle.

## 2 Experimental procedures

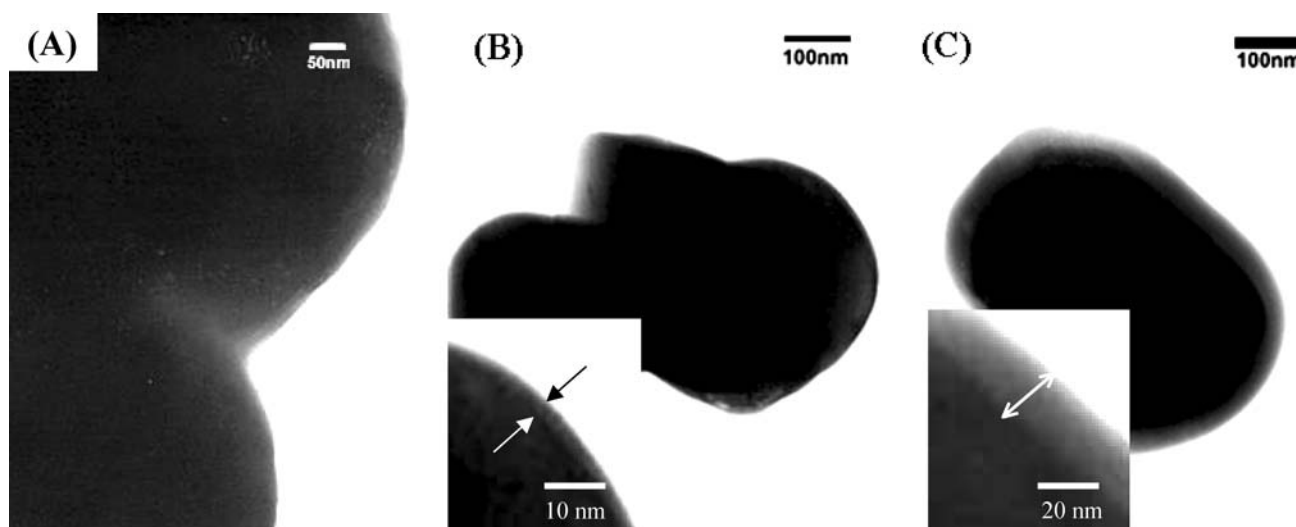
Barium titanate powders (BT-04B, Sakai Chemical Industry Co. Ltd., Japan, average diameter =  $0.4 \mu\text{m}$ ) and yttrium nitrate hexahydrate ( $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , Aldrich, 99.9%) were used to form a core-shell structure. Urea (Aldrich, 99+%) was used to provide carbonating ions for the synthesis of metal basic carbonates. Polyvinyl pyrrolidone (PVP,  $M_w = 40,000$ , Aldrich) was used as a stabilizer. Barium titanate powders were added to yttrium nitrate and urea solution, and then it was sonicated for 5 min to obtain homogeneous solution. Finally, PVP solution was added to the suspension, and the entire suspension was aged in a convection oven at  $90^\circ\text{C}$  for 6 h to initiate the formation of yttrium carbonate nuclei on the barium titanate surface. Unreacted compounds and PVP were removed by washing with fresh wa-

ter and ethanol. Particle size and morphology were investigated by transmission electron microscopy (TEM) (JEOL, JEM2000-EX II). Suspensions were prepared at a volume fraction of 0.1% solids by mixing  $\text{BaTiO}_3$  powder with a prepared 0.01 M  $\text{NaNO}_3$  solution. Ultrasonic treatment for 3 min was carried out to disperse the powder and suspensions were equilibrated for 12 hrs. The electrokinetic potential was determined by electroacoustic measurements as a function of pH using an ESA 9800 analyzer (Matec Applied Sciences, Hopkinton, MA). Details of this technique, its application to ceramic systems, and the estimated measurement precision, have been given previously [17, 18].

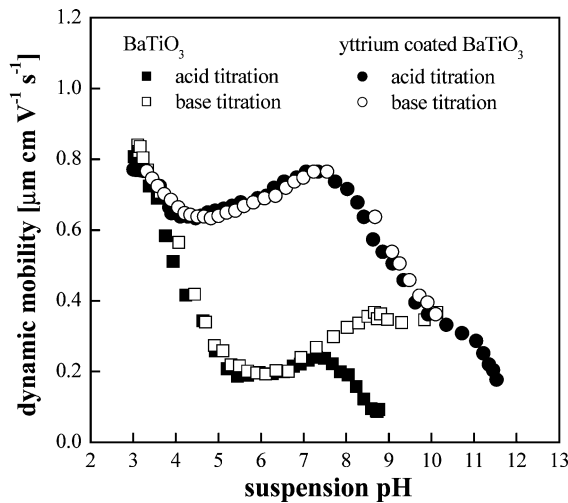
The dissolution of Y-coated  $\text{BaTiO}_3$  as a function of pH was determined by using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). On the basis of preliminary studies, the suspensions were adjusted with acid to reach target values from pH 9 to pH 3 after a 12 h equilibration period. Other suspensions were first adjusted to pH 3 and then subsequently adjusted with base to reach target values of pH 4, 7, 8, 9, and 10 after 12 h. Following the equilibration period, samples were centrifuged at 15,000 rpm for 30 min. Supernatants were clarified using a  $0.2 \mu\text{m}$  Acrodisc<sup>TM</sup> filter cartridge (Gelman Sciences, Ann Arbor, MI). ICP-AES analysis was performed on the clarified supernatant.

## 3 Results and discussion

Figure 1 shows TEM images of the coated particles as a function of yttrium nitrate concentration. The thickness of coating layer increases with the increase of the initial concentration of yttrium nitrate. A  $\sim 5 \text{ nm}$  thick yttrium carbonate layer was coated on the  $\text{BaTiO}_3$  particle at an yttrium



**Fig. 1** Morphologies of the coated particles at the following yttrium nitrate concentrations: (a) 0.5, (b) 1.0, and (c) 2.0 mM



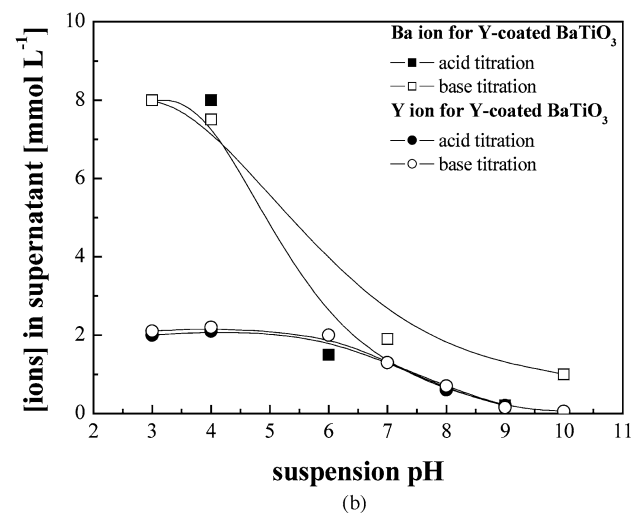
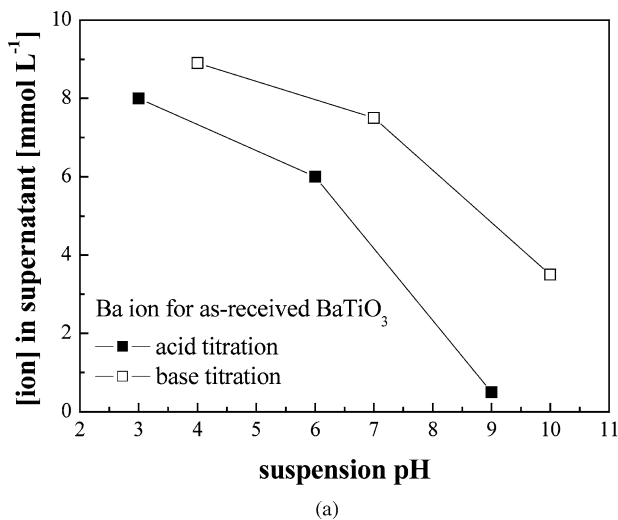
**Fig. 2** Electrokinetic behaviors of as-received and Y-coated BaTiO<sub>3</sub> particles during an acid and base titration as a function of suspension pH and titration direction

nitrate concentration of 1.0 mM as shown in Fig. 1(b). Y-coated BaTiO<sub>3</sub> prepared at an yttrium nitrate concentration of 2.0 mM yielded a ~ 20 nm thick yttrium carbonate layer on the BaTiO<sub>3</sub> particle as presented in Fig. 1(c). The atomic ratio of Ba and Y after Y coating determined by ICP-AES analysis indicated that ~80% of the original Y source had coated on the BaTiO<sub>3</sub> particle surface.

The electrokinetic behaviors of as-received BaTiO<sub>3</sub> and Y-coated BaTiO<sub>3</sub> are presented by the dynamic mobility curves shown in Fig. 2. At a volume fraction of 1%, both as-received and Y-coated BaTiO<sub>3</sub> powder did not exhibit a p*H*<sub>iep</sub>, remaining positively charged over the entire experimental pH range. Extrapolation of the leading portion of the acid titration curve indicated the native p*H*<sub>iep</sub> is near pH 9.0 and 12.0 for as-received and Y-coated BaTiO<sub>3</sub> powders, respectively. The dynamic mobility of Y-coated BaTiO<sub>3</sub> was

significantly higher than that of as-received BaTiO<sub>3</sub>. In the initial titration from pH 8.8 to pH 7, the dynamic mobility of as-received BaTiO<sub>3</sub> particle increased slightly. In the subsequent range, from pH 7 to pH 5.5, mobility decreased. From pH 5.5 to pH 3, the mobility steeply increased again. After completion of the acid titration, the suspension was then back-titrated to pH 10. In the region from pH 3 to pH 7, dynamic mobility closely followed the corresponding acid titration region. However, above pH 7, the electrokinetic behavior of BaTiO<sub>3</sub> displayed a significant hysteresis between acid and base portions of the titration cycle. One can conclude from these results that a significant modification of the BaTiO<sub>3</sub> surface has occurred during the initial acid titration, a modification that impacts the electrochemical state of the suspension. As shown in Fig. 2, in the initial titration from pH 11.5 to pH 7 the dynamic mobility of Y-coated BaTiO<sub>3</sub> increased drastically due to positively charged yttrium carbonate in the same pH region [8]. Conversely, mobility decreased in the subsequent pH range between 7 and 4. From pH 4 to pH 3, the mobility again increased slightly. In the base titration, the dynamic mobility of Y-coated BaTiO<sub>3</sub> closely followed the corresponding acid titration. The similarity between acid and base titration curves suggested that the starting surface component of Y-coated BaTiO<sub>3</sub> and the surface component following acid-base treatment remained the same.

In the as-received BaTiO<sub>3</sub>, Ba dissolution increased significantly as the treatment pH became more acidic, and the Ba concentration approached a maximum near pH 4 as shown in Fig. 3(a). A significant difference between the acidic and basic titrations was observed, which implied a modification of the surface structure and associated chemistry. On the contrary, in the Y-coated BaTiO<sub>3</sub>, Ba dissolution increased gradually until pH 6 during acid titration. Below pH 6, it increased steeply, and the dissolved Ba concentration approached a



**Fig. 3** Dissolved Ba and Y concentrations as a function of pH (a) BaTiO<sub>3</sub> (b) Y-coated BaTiO<sub>3</sub>

maximum near pH 4 as shown in Fig. 3(b). Y dissolution in basic environment increased with decreasing suspension pH, and the dissolved Y concentration reached a plateau near pH 6. The dissolution behavior of the Y ions during the base titration closely followed the corresponding acid titration. At and above pH 6, the Ba dissolution of Y-coated BaTiO<sub>3</sub> was significantly reduced compared to that of the as-received BaTiO<sub>3</sub>. This suggested that the presence of Y compounds on the BaTiO<sub>3</sub> particles retarded the dissolution of Ba ions from BaTiO<sub>3</sub>.

#### 4 Conclusion

The influence of a Y coating on the electrokinetic behavior and dissolution behavior of BaTiO<sub>3</sub> in an aqueous medium was investigated. The electrokinetic behavior of as-received BaTiO<sub>3</sub> exhibited a significant hysteresis between sequential acid and base portions of the titration cycle. On the contrary, this hysteresis of the electrokinetic behavior was not observed for Y-coated BaTiO<sub>3</sub>. It was revealed that this hysteresis was primarily the result of a pH-dependent Ba dissolution (surface depletion) and adsorption—precipitation of the dissolved Ba following a subsequent increase of the suspension pH. It can be concluded that the initial surface of the Y-coated BaTiO<sub>3</sub> and the surface after acid-base treatment was the same. Therefore, it was suggested that the coating retarded the dissolution of Ba ions from BaTiO<sub>3</sub>.

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#### References

1. J. Nowotny and M. Rekas, *Electronic Ceramic Materials*, edited by J. Nowotny, (Trans Tech, Zürich, Switzerland, 1992).
2. D.J. Shanefield, *Multilayer Ceramic Devices*, edited by J.B. Blum, (American Ceramic Society, Westerville, OH, 1986) p. 155.
3. D.A. Anderson, J.H. Adair, D. Miller, J.V. Biggers, and T.R. Shrout, *Ceramic Powder Science II*, edited by G.L. Messing, E.R. Fuller, Jr., and H. Hausner (American Ceramic Society, Westerville, OH, 1988) p. 485.
4. M.C. Blanco-Lopez, B. Rand, and F.L. Riley, *J. Euro. Ceram. Soc.*, **17**, 281 (1997).
5. S. Venigalla and J.H. Adair, *Chem. Mater.*, **11**, 589 (1999).
6. X.Y. Wang, S.W. Lu, B.I. Lee, and L.A. Mann, *Mater. Res. Bull.*, **35**, 2555 (2000).
7. D. Völtzke, H.-P. Abicht, J. Woltersdorf, and E. Pippel, *Mater. Chem. Phys.*, **73**, 274 (2002).
8. U. Paik and V.A. Hackley, *J. Am. Ceram. Soc.*, **83**, 2381 (2000).
9. U. Paik, S. Lee, and V.A. Hackley, *J. Am. Ceram. Soc.*, **86**, 1662 (2003).
10. J.S. Abel, G.C. Stangle, C.H. Schilling, and I.A. Aksay, *J. Mater. Res.*, **9**, 451 (1994).
11. S. Venigalla, D.J. Clancy, D.V. Miller, J.A. Kerchner, and S.A. Costantino, *Am. Ceram. Soc. Bull.*, **78**, 51 (1999).
12. J. Lee, K. Hong, and J. Jang, *J. Am. Ceram. Soc.*, **84**, 2001 (2001).
13. C. Hérard, A. Raivre, and J. Lemaître, *J. Eur. Ceram. Soc.*, **15**, 145 (1995).
14. S. Lee, U. Paik, V.A. Hackley, Y.-G. Jung, and K.-J. Yoon, *Materials Research Bulletin*, **39**, 93 (2004).
15. U. Paik, V.A. Hackley, J. Lee, and S. Lee, *J. Mater. Res.*, **18**, 1266 (2003).
16. T. Nomura and Y. Nakano, *Ceramic Transactions Vol. 131: Recent Developments in Electronic Materials and Devices*, edited by K.M. Nair, A.S. Bhalla, and S.I. Hirano, (The American Ceramic Society, Westerville, OH, 2002) Vol. 131, p. 87.
17. V.A. Hackley, U. Paik, B. Kim, and S.G. Malghan, *J. Am. Ceram. Soc.*, **80**, 1781 (1997).
18. V.A. Hackley, and U. Paik, *Ultrasonic and Dielectric Characterization Techniques for Suspended Particulates*, edited by V.A. Hackley and J. Texter, (American Ceramic Society, Westerville, OH, 1998) p. 191.