

Dispersion stability of ultra-fine BaTiO₃ suspensions in aqueous medium

M.P. Chun[†], Y.B. Chung, Y.J. Ma, J.H. Cho and B.I. Kim

Advanced Materials and Components Lab., Korea Institute of Ceramic Engineering and Technology, Seoul 153-801, Korea

(Received October 17, 2005)

(Accepted November 28, 2005)

Abstract The effect of pH and particle size on the dispersion stability of ultra-fine BaTiO₃ suspensions in aqueous medium have been investigated by means of zeta potential, sediment experiments, and powder properties (particle analysis, specific surface area) etc. Zeta potential as a function of pH for two particles of different size increases from -75 to +10 mV with decreasing pH from 8.5 to 1.4. The curve of zeta potential for small particle (150 nm) has slow slope than that of large particle (900 nm), giving IEP (isoelectric point) value of pH = 1.6 for small particle and pH = 1.9 for large particle respectively, which means that it is more difficult to control zeta potential with pH for small particle than large particle. The dispersion stability of BaTiO₃ particles in aqueous medium was found to be strongly related with the agglomeration of colloidal suspensions with time through the sedimentation behaviors of colloidal particles with time and pH value.

Key words BaTiO₃, Dispersion, Suspension, Zeta potential, Sedimentation, IEP

1. Introduction

Barium titanate (BaTiO₃) has been used as capacitor, positive temperature coefficient of resistivity (PTCR) [1, 2] and electro-optic materials due to its excellent dielectric, semi-conducting and transparent properties. In particular, multilayer ceramic capacitor (MLCC) with a high capacitance such as X7R and Y5V is usually manufactured using this material of high dielectric constant. With the miniaturization and high performance of electronic components and devices, the number of stacking layer increases and the dielectric thickness decreases for MLCC. To manufacture MLCC of which dielectric layers is less than 2.5 μm, Ultra-fine powders should be used for improving the reliability of MLCC. However, ultra-fine powders are intended to agglomerate due to their large specific surface area and it is difficult to make well-dispersed solution of these particles.

The uniform dispersion of BaTiO₃ particles in liquid medium is very important for attaining the desirable green sheet, as well as for producing defect free dielectric layers. Therefore, many researches [3-10] with regard to the dispersion of BaTiO₃ particles in an aqueous and non-aqueous medium have been conducted. Generally, the dispersant is used to make the fine particles of barium titanate stabilized suspensions in aqueous medium via an electrostatic repulsion or steric hinderance [11]. In this

work, to understand the dispersion stability of ultra-fine BaTiO₃ suspensions in aqueous medium, zeta potential, sediment experiments are conducted, and powder properties are measured at different pH value and particle sizes.

2. Experimental

Barium titanate powders (Sakai chemical) nominated by powder A and powder B of two different sizes were used as starting materials. Particle sizes and specific surface areas were measured by laser light scattering method (LA910, Horiba) and BET method (Tristar3000, Micromeritics), respectively. From these measurement, large powder A has a specific surface area of 13.5 m²/g, particle size (D₅₀) of 150 nm and small powder B has a specific surface area of 3.0 m²/g, particle size (D₅₀) of 900 nm. Figure 1 shows the SEM micrographs of BaTiO₃ powders. It should be noticed that the shape of particles is roughly spherical and some size distribution of particles is shown with particle agglomerations.

In order to measure the zeta potential and sedimentation behavior of barium titanate powders, very dilute aqueous suspensions of BaTiO₃ are required. They were prepared through the following procedure. The BaTiO₃ powders of 0.01 g were mixed with the distilled water of 200 ml and the dispersant of 0.01 wt% (Darvan C, Dupont) were added into this solution. After that, the samples were ultrasonicated for 30 min. The pH of aqueous solutions was adjusted via addition of HCl and NH₄Cl. Then, the zeta potentials were measured using laser

[†]Corresponding author
Tel: +82-2-3282-2429
Fax: +82-2-3282-2430
E-mail: myoungpyo@kicet.re.kr

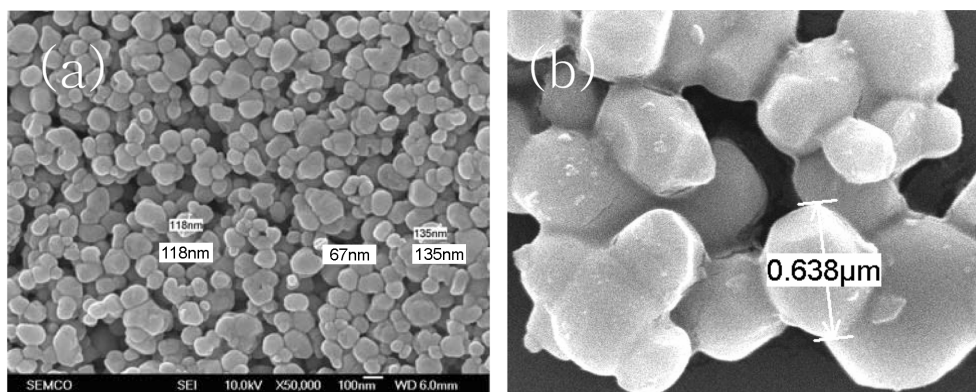


Fig. 1. SEM micrographs of (a) Powder A ($D_{50} = 150$ nm, $BET = 13.5$ m²/g), and (b) Powder B ($D_{50} = 900$ nm, $BET = 3.0$ m²/g).

Doppler method (ELS-8000, Ostuka) and sedimentation experiments (Turbiscan, Formulacion) were conducted with measuring the scattering (transmission and reflection [12, 13]) intensity of the light source due to aqueous suspensions as a function of time and pH value. SEM micrographs of the settled particles were investigated to understand the sedimentation mechanism of aqueous suspensions.

3. Results and Discussion

3.1. Zeta potential

In order to investigate the effect of particle size on the dispersion stability of aqueous BaTiO₃ suspensions, zeta potential as a function of pH was measured for two powders of different size as shown in Fig. 2. It is shown that zeta potential increases from -75 to 10 mV with decreasing pH from 8.5 to 1.4. As the pH value of

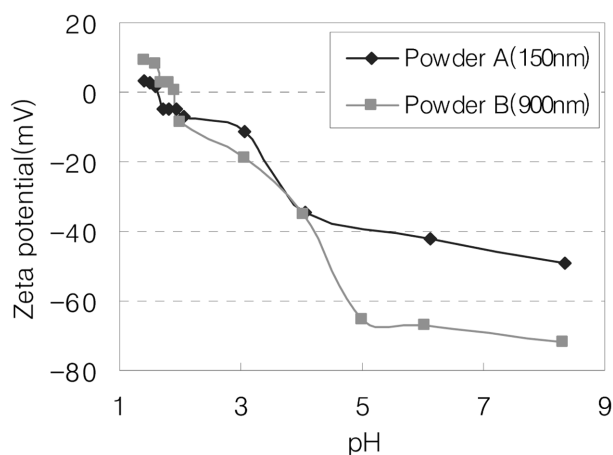


Fig. 2. Variation of zeta potential as a function of pH for two different powders (Powder A, B).

aqueous solution decreases, zeta potential increases rapidly near pH of 4 for powder A, and pH of 5 for powder B, respectively. Similar result was also reported in the literature [14]. It is interesting to note that the IEP increases with increasing particle size, from 1.6 for powder A (150 nm) to 1.9 for powder B (900 nm), which is lower in comparison with literatures [15-17]. Since the variation of zeta potential as a function of pH for small powder is slower than that for large powder, zeta potential of small powder is higher than that of large one on the high side of pH value, while on the lower side of pH value, zeta potential of small powder is lower than that of large one. These results are considered to be due to the difference of specific surface area as well as the number of particles between powder A and powder B.

3.2. Sedimentation

The gravity-settling behavior of BaTiO₃ suspensions was studied by measuring the transmission of the light source through the aqueous suspensions as a function of time for different pH values and powders. Figure 3. shows the variation of transmission intensity along the height of sample tube at various time during the settling of the aqueous suspensions of powder A with pH of 1.6 (a) and pH of 7.6 (b). As shown in Fig. 3 (a), the intensity of transmission for the suspensions of pH = 1.6 increase quickly, which means the particle agglomeration and sedimentation due to low zeta potential. However, the transmission for the suspensions of pH = 8.3 is observed to be rather constant as shown in Fig. 3(b), which means the stabilization of suspensions [18, 19]. It should be noticed that the lower the pH is, the less stable is the aqueous suspensions. Figure 4. shows the variation of transmission intensity along the height of the sample tube at various time during the settling of the

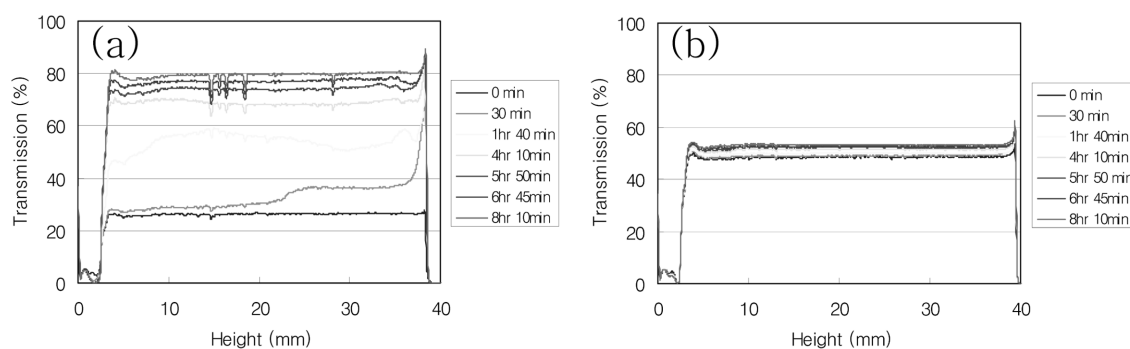


Fig. 3. Variation of transmission intensity as a function of the height of the sample tube at various time during the settling of the aqueous suspensions of powder A with pH of 1.6 (a) and pH of 8.3 (b).

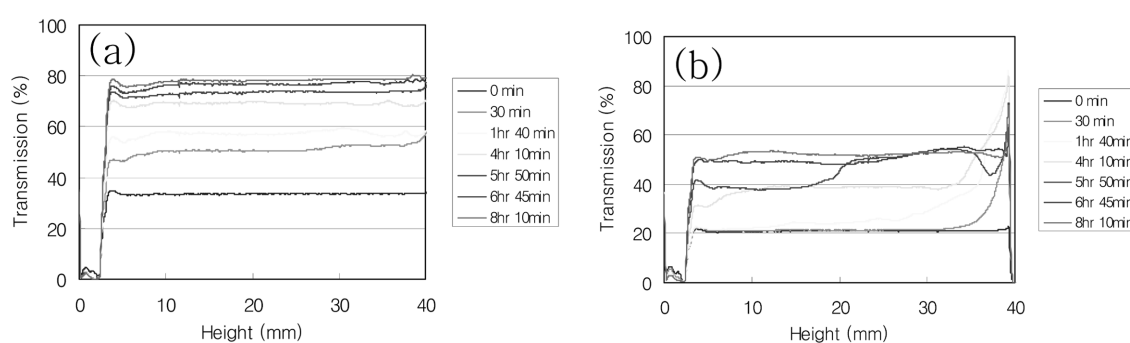


Fig. 4. Variation of transmission intensity along the height of the sample tube at various time during the settling of the aqueous suspensions of powder B with pH of 1.9 (a) and pH of 7.6 (b).

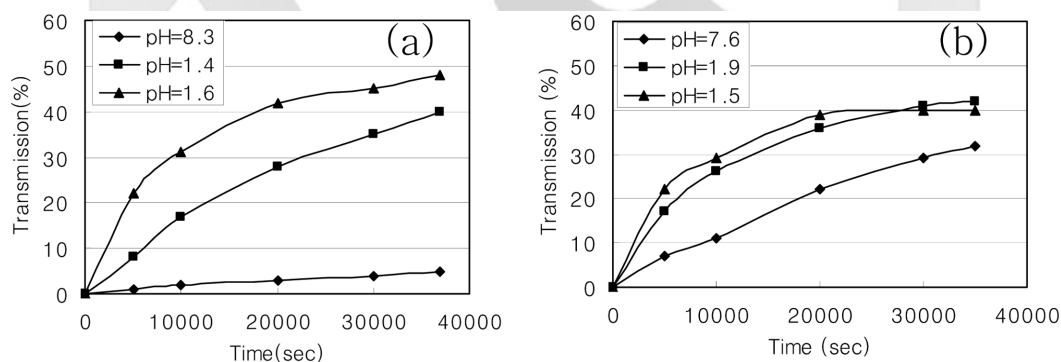


Fig. 5. Variation of transmission intensity as a function of time for the aqueous suspensions of powder A (a) and powder B (b).

aqueous suspensions of powder B with pH of 1.9 (a) and pH of 7.6 (b). The rapid increase of the transmission intensity for powder B of pH = 1.9 was observed as shown in Fig. 4(a), which is a similar result with powder A of pH = 1.6. The variation of transmission intensity for powder B of pH = 7.6 increases rapidly as a function of time and such a result is quite different from that of powder A of pH = 8.3. The reason why the suspensions of powder B with pH = 7.6 is not stabilized and settles down seems to be due to the larger particle size of powder B than that of powder A. Figure 5(a) and (b) shows the variation of transmission

intensity as a function of time for two powder A and B at different pH values. As the time elapses, the transmission intensity increases continuously owing to the sedimentation of the suspensions and the rate by which the transmission changes increases with decreasing pH value.

To investigate the effect of pH and particle size on the dispersion stability of aqueous BaTiO₃ suspensions, the particle packing of the sediments which settled out of aqueous suspensions was observed by using SEM. Figure 6(a) and (b) shows SEM micrographs of the sediments settled from suspensions of powder A with low

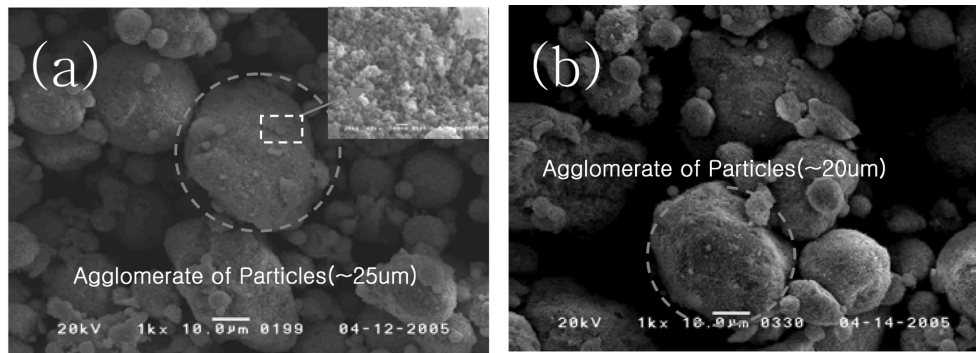


Fig. 6. SEM micrographs of the aqueous suspensions settled on the bottom of sample tube for powder A with pH of 1.6 (a) and pH of 8.3 (b).

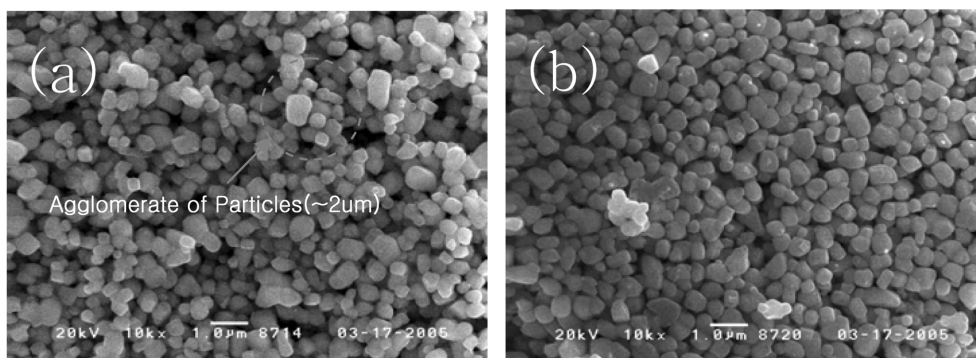


Fig. 7. SEM micrographs of the aqueous suspensions settled on the bottom of sample tube for powder B with pH of 1.9 (a) and pH of 8.3 (b).

and high pH. In Fig. 6(a) and (b), only very large agglomerates composed of ultra fine particles are shown and the size distribution of agglomerates is broad from 1 to 25 μm . As any particles which do not flocculate each other were not observed for the sediments of powder A, they are likely to be stabilized aqueous suspensions. Therefore, the sedimentation mechanism of ultra fine particle (150 nm) is considered to be due to the coalescence of particles and settling down. Figure 7(a) and (b) shows SEM micrographs of sediments settled from suspensions of powder B with low and high pH. Some voids larger than the particle size are present and several surface area of sediments shows the rough packing and agglomerates of particles for suspensions of low pH = 1.9 as shown in Fig. 7(a), whereas for suspensions of high pH = 8.3, ideal close packing of particles are shown without agglomeration in Fig. 7(b), which means that the aqueous suspensions composed of large particles can not be stabilized with time in spite of well dispersion of particles in aqueous medium. Coalescence and settling of particles down is considered to occur simultaneously for the sedimentation of large particle (900 nm).

4. Conclusions

In order to investigate the effect of particle size and pH on the dispersion stability of aqueous BaTiO_3 suspensions, zeta potential and sedimentation experiments were conducted and SEM micrographs of sediments were observed. It was observed that zeta potential increases with decreasing pH, but zeta potential increases rapidly below some pH value. For IEP, large powder A (150 nm) was pH = 1.64 and small powder B (900 nm) was pH = 1.94. Sedimentation experiments were conducted with measuring the light scattering (transmission and reflection) intensity of the light source due to aqueous suspensions in sample tube. The transmission intensity increases continuously with elapsed time. From the analysis of sedimentation behavior and the observation of particle packing of sediments, the sedimentation mechanism of ultra fine particle (150 nm) is considered to be due to the coalescence of particles and settling down. However, for large particle (900 nm), the coalescence and sedimentation of particles was considered to occurs simultaneously. Also, it seems that the aqueous suspensions composed of large particles (900 nm) can not be stabilized with time.

References

- [1] D. Hennings, C. Metzmacher and B. Schreinemacher, "Defect chemistry and microstructure of hydrothermal barium titanate", *J. Am. Ceram. Soc.* 84 (2001) 179.
- [2] M. Buscaglia, V. Buscaglia, M. Viviani, P. Nanni and M. Hanuskova, "Influence of foreign ions on the crystal structure of BaTiO₃", *J. Eur. Ceram. Soc.* 20 (2000) 1997.
- [3] U. Paik, V. Hackley, S. Choi and Y. Jung, "The effect of electrostatic repulsive forces on the stability of BaTiO₃ particles suspended in non-aqueous media", *Coll. Surf. A* 135 (1998) 77.
- [4] D. Kim, J. Yeo, Y. Jung, S. Choi and U. Paik, "Suspension stability and consolidation behavior of ultrafine BaTiO₃ particles in nonazeotropic solvent system", *Mater. Chem. Phys.* 82 (2003) 181.
- [5] W.J. Tseng and C. Lin, "Effect of dispersants on rheological behavior of BaTiO₃ powders in ethanol-isopropanol mixtures", *Mater. Chem. Phys.* 80 (2003) 232.
- [6] X. Wang, B. Lee and L. Mann, "Dispersion of barium titanate with polyaspartic acid in aqueous media", *Coll. Surf. A* 202 (2002) 71.
- [7] W.J. Tseng, "Rheology of colloidal BaTiO₃ suspension with ammonium polyacrylate as a dispersant", *S. Li, Mater. Sci. Eng. A* 333 (2002) 314.
- [8] Z. Chen, T. Ring and J. Lemaitre, "Stabilization and processing of aqueous BaTiO₃ suspension with polyacrylic acid", *J. Am. Ceram. Soc.* 75 (1992) 3201.
- [9] B. Lee, "Chemical variation in barium titanate powders and dispersants", *J. Electroceram.* 3 (1999) 53.
- [10] G. Carlos, B. Heberto and M. Froylan, "Colloidal processing of BaTiO₃ using ammonium polyacrylate as dispersant", *Ceram. Int.* 26 (2000) 609.
- [11] D. Liu, "Rheology of aqueous suspensions containing highly concentrated nano-sized zirconia powders", *J. Mater. Sci. Lett.* 17 (1998) 1883.
- [12] O. Mengual, G. Meunier, I. Cayre, K. Puech and P. Snabre, "Characterization of instability of concentrated dispersions by a new optical analyzer: the Turbiscan MA 1000", *Coll. Surf. A* 152 (1999) 111.
- [13] C. Chauvierre, D. Labarre, P. Couvreur and C. Vauthier, "A new approach for the characterization of insoluble amphiphilic copolymers based on their emulsifying properties", *Coll. Polym. Sci.* 282 (2004) 1097.
- [14] W. Luan and L. Gao, "Influence of pH value on properties of nanocrystalline BaTiO₃ powder", *Ceram. Int.* 27 (2001) 645.
- [15] J.H. Jean and H.R. Wang, "Dispersion of aqueous barium titanate suspensions with ammonium salt of poly(methacrylic acid)", *J. Am. Ceram. Soc.* 81 (1998) 1589.
- [16] M.C. Blanco Lopez, B. Rand and F.L. Riley, "The properties of aqueous phase suspensions of barium titanate", *J. Euro. Ceram. Soc.* 17 (1997) 281.
- [17] W.S. Cho and E. Hamada, "Synthesis of ultrafine BaTiO₃ particles from polymeric precursor: their structure and surface property", *J. Alloys and Compounds* 266 (1998) 118.
- [18] Z. Shen, J. Chen, H. Zou and J. Yun, "Dispersion of nanosized aqueous suspensions of barium titanate with ammonium polyacrylate", *J. Coll. Int. Sci.* 275 (2004) 158.
- [19] J. Zhao, X. Wang, Z. Gui and L. Li, "Dispersion of barium titanate with poly(acrylic acid-co-maleic acid) in aqueous media", *Ceram. Int.* 30 (2004) 1985.