Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Journal of the European Ceramic Society 23 (2003) 1901–1910

www.elsevier.com/locate/jeurceramsoc

Preparation of nanometer-sized barium titanate powders by a sol-precipitation process with surfactants

Kun-Ming Hung[a,*], Wein-Duo Yang[a,b], Chia-Chia Huang[a]

[a]Department of Chemical Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 80807, Taiwan, ROC
[b]Materials Science 138-78, California Institute of Technology, Pasadena, CA 91125, USA

Received 29 March 2002; received in revised form 4 November 2002; accepted 11 November 2002

Abstract

Nanometer sized barium titanate powders can be obtained by adding surfactants to titanyl acylate precursors in a strong alkaline solution ($pH > 13$). FTIR, TGA, SEM and XRD were used to investigate the effects of the surfactants influence on the morphology of the obtained titanate powders and their sinterability. In a pre-added surfactant process (i.e. surfactant added before precipitation in alkaline solution), a slower rate of hydrolyzation is observed, and the shift rate in the condensation is slower. Less crosslinking of smaller particles is observed. The addition of anionic surfactant (LAS) in general leads to the formation of micelles, which control the nucleation and crystal growth of the titanate powders. This micelle formation results in a smaller particle size (30–90 nm), and a larger surface area of 60.5 m^2/g for $BaTiO_3$ powders was obtained. The nanometer-sized barium titanate powders were readily sintered at 1100–1200 °C.

Keywords: $BaTiO_3$; Powders: chemical preparation; Sol-gel processes; Surfactants

1. Introduction

Barium titanate crystallizes in a perovskite structure is an important electronic ceramic. Semiconducting properties can be achieved by doping it with La^{3+}[1] or Nb^{5+}[2] as the heterovalent element or through sintering in a reducing atmosphere.[3] The titanates semiconducting and dielectric properties can be controlling by the grain boundary, and are widely applied for use in photoelectrodes,[4] multilayer chip capacitor (MLCC),[5] positive temperature coefficient resistance (PTCR) heater and sensors,[6] embedded capacitance[7] and devices of various boundary-layer capacitors.[8] For the rapidly progressing development of very large scale integrated (VLSI) circuits, high purity nanometer-sized powders are required for manufacturing an electronic device of high capacity.[9]

In the preparation of barium titanate from the expensive titanium alkoxide a high molecular weight gel is easily formed by reaction with the moisture of atmosphere.[10] This gel is not very soluble which affects the quality of the product.[11] The titanyl acylate precursor, made by chelating the titanium alkoxide with acetic acid, can be dissolved in water and reacts readily with the alkali earth metal ion to form a clear and homogeneous solution. Barium titanate powder is produced by adding a strong alkaline solution ($pH > 11$) to the above solution.[12–14] The process of forming the perovskite powder directly in a strong alkaline solution has the advantages of low temperature and excellent compositional homogeneity of the powder, making it an ideal method. However, Kao and Yang[15] have proposed a modified sol-precipitation method to prepare nanometer-sized strontium titanate powder from a titanyl acylate precursor in a strong alkaline solution. They discovered that during the sol-precipitation process the strontium ion diffused into the gel formed through hydrolysis of the titanyl acylate precursor. The physical and chemical properties of the $SrTiO_3$ powder are controlled by the morphology of the preceding titanyl acylate precursor. The hydrolysis and polycondensation control the morphology of the titanyl acylate precipitate, and are therefore the crucial steps in obtaining the desired end product.

Atoms or molecules adsorbed on the surface of the $BaTiO_3$ powders, change its surface characteristics.

---

* Corresponding author.
E-mail address: master@cc.kuas.edu.tw (K.-M. Hung).

0955-2219/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0955-2219(02)00431-4

Hence, absorption phenomena always noted during the manufacturing process of the ceramic are crucial for attaining the desired product characteristics. Surfactants could be used to improve the quality of the ceramic. Hence, the effects of organic additives on the colloidal stability of aqueous $BaTiO_3$ suspensions have been investigated.[16,17] Kiss[18] has prepared a $BaTiO_3$ powder, using some additive and controlling the polarity of the solvent thereby obtained a high-purity $BaTiO_3$ powder. Furthermore, Potdar et al.[19] have studied the effects of an anionic surfactant sodium dodecyl sulphate (SDS) during precipitation of the molecular precursor, barium titanyl oxalate (BTO) in the preparation of $BaTiO_3$. They revealed that addition of SDS helps in production of dispersed, spherical cubic $BaTiO_3$ powder. Additionally, Xu et al.,[20] also found that nanometer ZnO gas sensing material with different size has been controlled by the selecting proper surfactants and preparation process.

In the present study, we prepared nanometer sized $BaTiO_3$ powders by using three different surfactants (anionic, cationic and nonionic) for the titanyl acylate precursor. Combined FTIR, TGA, SEM and XRD etc. methods were used to investigate the effects on the morphology of the precursor and the influence of the surfactants on the particle size, sinterability and grain properties of the powder.

2. Experimental

2.1. Preparation of titanyl acylate precursor

15.0 ml titanium isopropoxide [$Ti(O\text{-}i\text{-}C_3H_7)_4$, density 0.995 g cm^{-1}, purity 98%] was brought to react with 28 ml of acetic acid (molar ratio $HOAc/Ti = 10$) to obtain a titanyl acylate precursor [$Ti(OAc)_x(O\text{-}i\text{-}C_3H_7)_y$]. In an exothermic reaction, 50 ml of degassed water was added and the mixture stirred vigorously causing the hydrolyzed titanyl acylate to form a clean solution. The steps were carried out at room temperature.

2.2. Sol-precipitate synthesis

The above hydrolyzed titanyl acylate precursor was mixed with 150 ml of 5 M NaOH ($pH > 13$). Through hydrolysis and polycondensation the solution formed a white precipitate. During the process, about 20 mg of surfactant [BKC (a cationic surfactant), Tween-20 (a nonionic surfactant) or LAS (an anionic surfactant)] was added to the solution either before (pre-added surfactant process) or after (post-added surfactant process) the formation of the precipitate. The precipitate was brought to reaction with 50 ml 1 M barium acetate solution containing $[Ba^{2+}]/[Ti^{4+}] = 1.00$ at boiling point (about 102–105 °C) for 2 h. The preparatory conditions for the precursors used to form nanometer-sized barium titanate are listed in Table 1. The excess mother liquor was filtered, and the obtained filter cake washed with degassed water at least three times to produce white nanometer-sized $BaTiO_3$ powder, containing less than 100 ppm of sodium ions. This white $BaTiO_3$ powder was then freeze-dried for 24 h.

2.3. Characterisations

In order to understand the influence of the surfactants, the hydrolyzed titanyl acylate precursors containing surfactant precipitated in a strong alkaline solution were filtered and collected in 3 min, cooled on an ice bath, washed with water and then dried in an oven at 105 °C for 24 h. Thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR) were used to analyze the precursors. Scanning electron microscopy (SEM) was used to analyze the microstructures of the precipitates and $BaTiO_3$ powders. X-ray diffraction (XRD) was used to characterize the perovskite phase. The specific area and pore size of powders were measured by N_2 adsorption–desorption isotherms at −196 °C on a Micromeritics ASAP 2010 analyzer.

After calcining and grinding through a mesh (<53 μm) the powders were pressed at 110 MPa in a stainless

Table 1
Preparatory conditions and powder properties of the nanometer-size $BaTiO_3$ prepared from various surfactants

Sample	Surfactant	Procedure	Particle size (nm) by SEM	BET surface area (m^2/g)	BET size[a] (nm)	Ratio of average particle size/BET size
(S1)	Without	–	70–120	16.2	62	1.5
(S2)	BKC	Before ppt	50–130	27.7	36	2.5
(S3)	Tween-20	Before ppt	60–110	22.5	44	1.9
(S4)	LAS	Before ppt	30–90	60.9	16	3.7
(S5)	BKC	After ppt	80–100	24.2	41	2.2
(S6)	Tween-20	After ppt	70–90	25.8	39	2.0
(S7)	LAS	After ppt	40–160	26.5	38	2.6

[a] The BET sizes were calculated by $d_{BET} = 6/(\rho \cdot S_{BET})$, where ρ is the theoretical density of $BaTiO_3$, is about 6 g/cm^3.

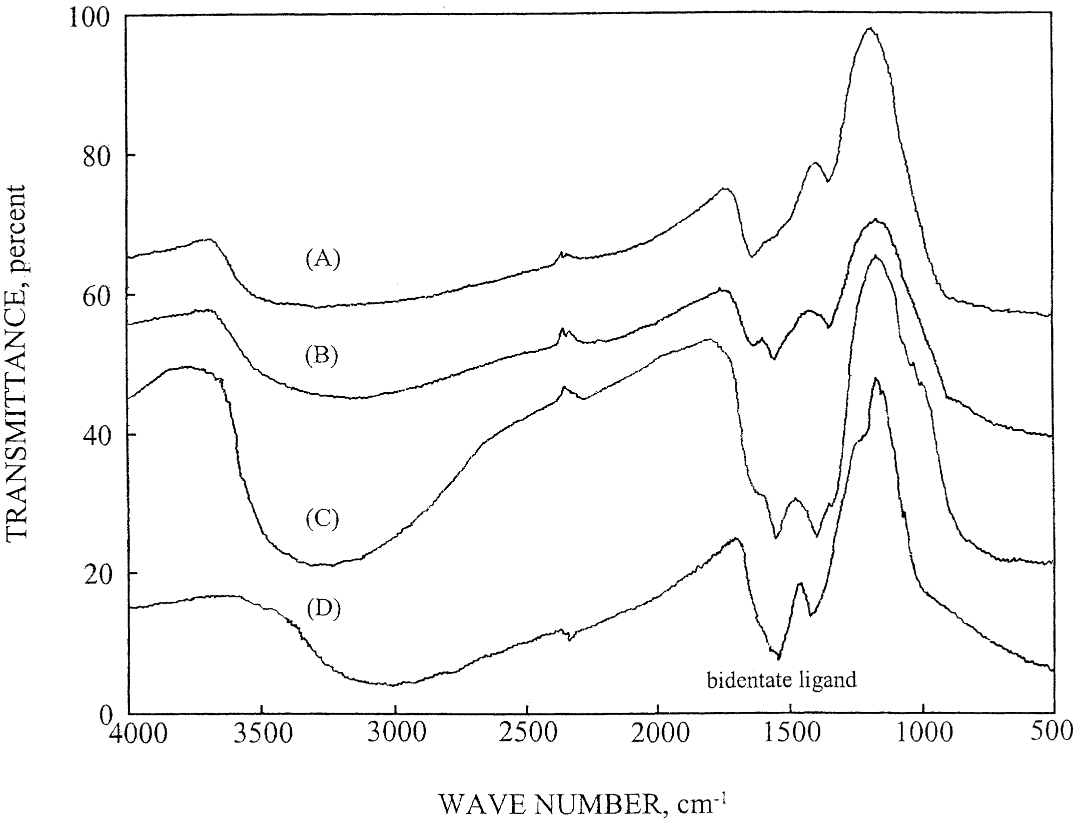


Fig. 1. The precipitates' FTIR spectra with surfactant added before the precipitation. Precipitates obtained from (A) without any surfactant added, (B) BKC surfactant added, (C) Tween-20 added, and (D) LAS surfactant added.

steel mold to form disk-like green bodies with a diameter of 13 mm and a thickness of 4–5 mm. Dilatometry was used to study the sinterability of the green bodies at a heating rate of 10 °C/min.

3. Results and discussion

3.1. The studies of titanyl acylate precipitates

3.1.1. FTIR analysis

The FTIR spectra of the various titanyl acylate precipitates in alkaline solution are shown in Fig. 1. It shows the precipitates' FTIR spectra with surfactants added before the precipitation. The acetate ligand chelating the titanium compound has two absorption bands near 1420 cm^{-1} and 1560 cm^{-1}, respectively. These two absorption bands are caused by symmetric and asymmetric vibrations of the acetate group [21]. When the difference of the two absorption peaks ($\Delta\nu$) is larger than 160 cm^{-1}, the acetate group is a typical bridging bidentate ligand. When it is smaller than 80 cm^{-1}, it is a chelating bidentate ligand. The spectra indicate that acetate still exists in the structure of the gel formed from the hydrolyzed titanyl acylate precursor in the solution at pH >13.

The FTIR spectra also show that the acetate group chelates with the titanium compound obtained from the precursor when different surfactant were added. The FTIR-spectrum of the starting material without any surfactant added [Fig. 1(A)] shows the bidentate ligand difference to be $\Delta\nu = 280$ cm^{-1}, which indicates a bridging bidentate ligand. This bridging bidentate ligand is responsible for a higher rate of crosslinking and a larger particle size. When LAS (an anionic surfactant) was added to the starting material the precipitate formed had a bidentate ligand difference of $\Delta\nu = 145$ cm^{-1}. This was the smallest bidentate ligand difference observed [see Fig. 1(D)] and indicates a more chelating bidentate ligand, resulting in a lower rate of crosslinking and a smaller particle size. The bidentate ligand difference $\Delta\nu$ of the precipitate obtained from the precursors where Tween-20 (a nonionic surfactant) was added $\Delta\nu = 150$ cm^{-1}. It is worthy to know that there are three absorption bands in the range of 1300–1600 cm^{-1} observed from BKC (a cationic surfactant) added as shown in Fig. 1(B). The broader linewidth and three shoulders show that two bidentate ligands were found at $\Delta\nu = 280$ cm^{-1} and $\Delta\nu = 155$ cm^{-1}, respectively, suggest that both chelating bidentate and bridging bidentate ligands should occur.[22] The absorption peaks of Ti–OR are found between 1000 and 1100 cm^{-1} in some of the four cases, therefore the gels obtained from the precursors still contained traces of Ti(OR)$_4$.[23]

In the cases of the three surfactants were added after precipitation the bidentate ligand difference was not markedly different and was in all cases close to $\Delta\nu$ about 280 cm^{-1} (not shown), the same as observed without a surfactant added. Comparing the pre-added process and the post-added process, it can be stated that adding surfactants before precipitation results in a smaller particle size of the resulting gel due to the chelating bidentate nature of the ligands. This lowers the crosslinking rate and reduces the particle size more than the addition of surfactants after precipitate.

3.1.2. TGA analyses

Fig. 2 shows the result of TGA analysis of the various titanyl acylate precipitates obtained by adding the different surfactants. The figure shows the weight change on heating up to 700 °C. The weight loss in the range 300–600 °C can be assumed to be representative of the amount of acetate groups in the titanyl acylate precipate. The precipitate obtained without adding any surfactant has ~1% [curve (A)] the least weight loss. If surfactant LAS was added before precipitation the highest weight loss, about 12% [curve (D)] was observed. The precipitates obtained by adding Tween-20 and BKC before precipitation resulted in a weight loss of 3% and 1%, respectively.

Combining the results of the FTIR and TGA studies, it can be concluded that the higher presence of the acetate ligand in the LAS anionic surfactant results in an inhibition of the hydrolysis reaction. Acetate inhibits the process of condensation, extends the gelation time,[24] and results in much smaller particles of the precipitate. In contrast, the amount of acetate groups is small in the precipitate without any surfactant added, so the hydrolysis reaction is more rapid, resulting in larger particles of the gel precipitate. The TGA graph also indicated that for the precursors obtained with surfactants added after precipitation, the weight loss between 300 and 600 °C of the four samples is almost the same at about 1–3%. This observation is in accordance with the FTIR analysis, which showed that surfactant addition after precipitation doesn't alter the mode of hydrolysis and polycondensation of precipitate precursors.

3.1.3. Electron microscopy of the titanyl acylate precipitates

The SEM images of the different precipitates obtained through pre-added surfactants in the strong alkaline solution are examined and shown in Fig. 3. It shows a serious agglomeration of the precipitated gels obtained

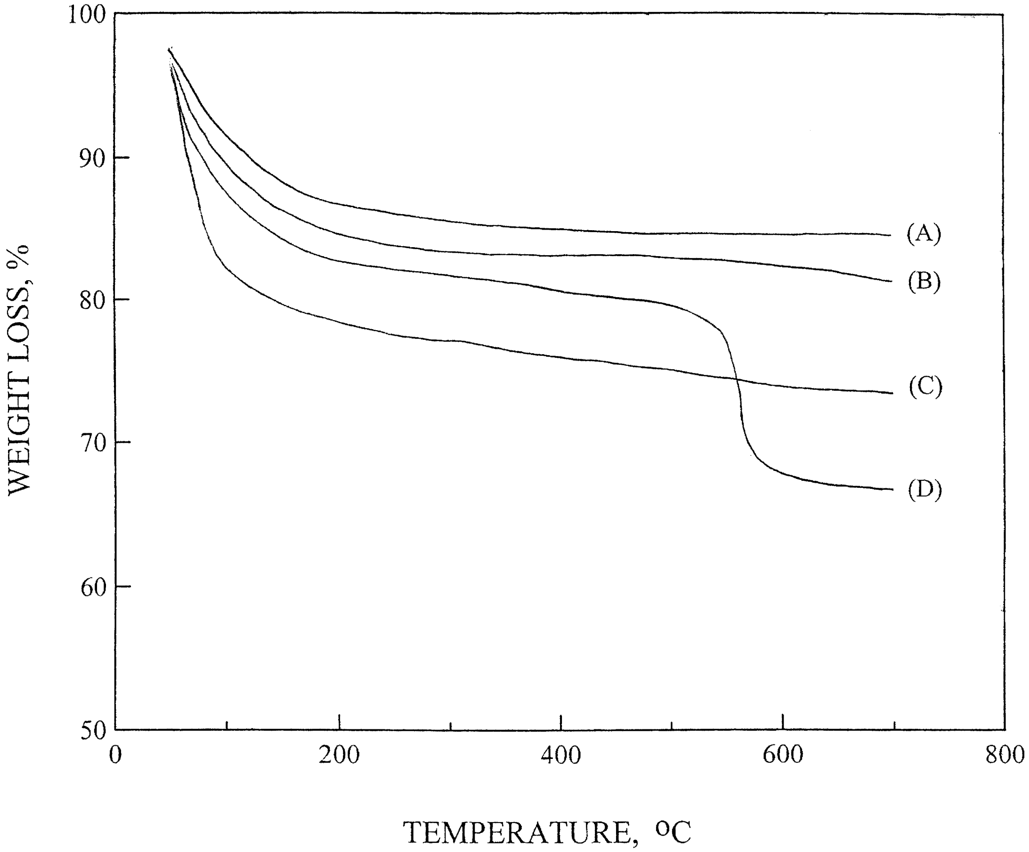
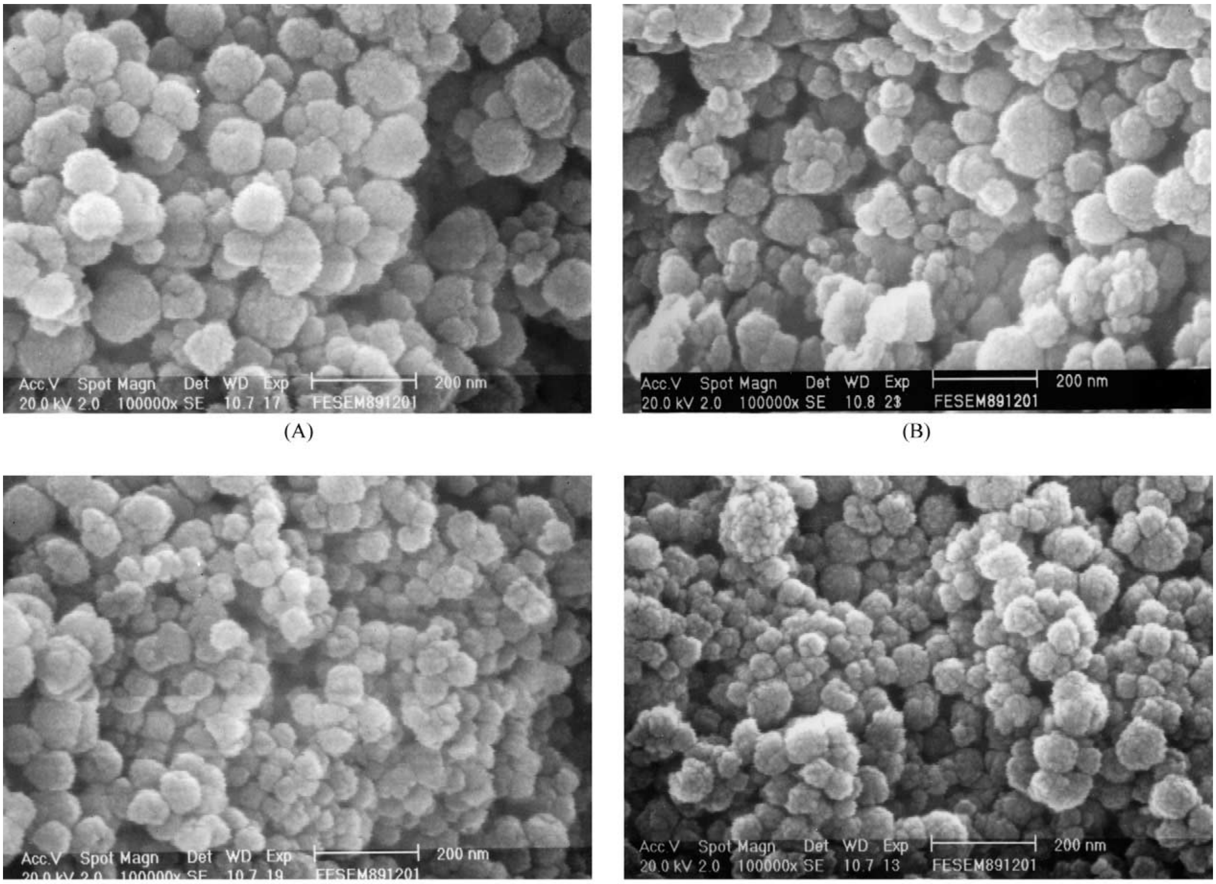


Fig. 2. Results of TGA analysis of the various titanyl acylate precipitates obtained by adding different surfactants before precipitation: (A) without any surfactant added, (B) BKC surfactant added, (C) Tween-20 added, and (D) LAS surfactant added.



(A) (B) (C) (D)

Fig. 3. SEM analysis of the titanyl acylate precipitate obtained through pre-added surfactant: (A) without any surfactant added, (B) BKC surfactant added, (C) Tween-20 added, and (D) LAS surfactant added.

from the titanyl acylate. The particles of the pre-added LAS precursor formed within 3 min, and are the finest, at about 40–70 nm. This is due to the fact that the rate of formation of the precipitate is the slowest in this case. The precipitates of the pre-added surfactants BKC and Tween-20, showed the particle sizes are 60–100 nm and 50–90 nm, respectively. The particle size of the precipitate without any surfactant added is about 70–120 nm, larger than that of any precipitates with surfactants. This is due to the reduction of the rate of polycondensation by added surfactants. The electron microscopy imagines of the precipitates with post-added surfactants were also examined. In these cases the particle sizes are all similar.

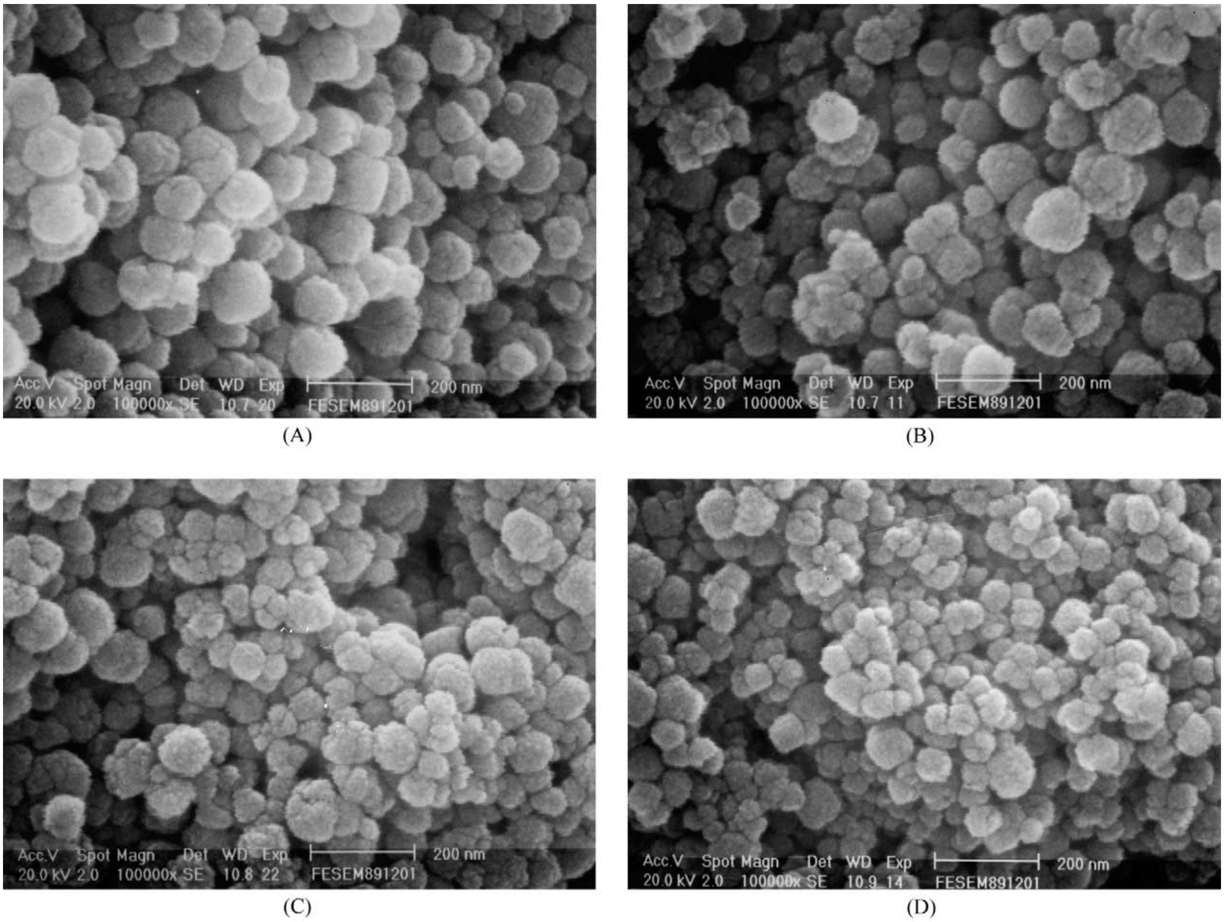
FTIR, TGA and electron microscopy studies show that the precipitated gel obtained from titanyl acylate precursor in alkaline solution is a polymer of chelating acylate with the titanium compound, and the resulting morphology is dependent on the acetate content of chelating in the precursor. The surfactants added before precipitation result in less crosslinking during the polycondensation process, i.e., the chelating bidentate ligand slows polycondensation and a precipitate with a small particle size is formed.

3.2. Powder characterization

3.2.1. Size of the powder particles

The nanometer-sized perovskite powders obtained through the pre-added surfactant process [powders (S1), (S2), (S3) and (S4)] were examined by SEM (Fig. 4). The particle size of the powder made without a surfactant added is again the largest (70–120 nm), as Fig. 4(A) shows, and that of the powder formed with LAS as a surfactant added is again the smallest (30–90 nm). However, the powders made from Tween-20 and BKC also have small particle sizes, 60–110 and 50–130 nm respectively.

Barium titanate powders were also obtained from different precursors with post-added surfactants (Fig. 5). The particle sizes of the powders obtained from the various surfactants were not much improved from the process of without a surfactant, about 30–160 nm. The particle size of the powder made with LAS as a surfac-



(A) (B)

(C) (D)

Fig. 4. SEM analysis of the nanometer-sized $BaTiO_3$ powder obtained through pre-added surfactant: (A) without any surfactant added, (B) BKC surfactant added, (C) Tween-20 added, and (D) LAS surfactant added.

tant added is again the smallest (40–160 nm), as Fig. 5(C) shows. The powders made from Tween-20 and BKC also have small particle sizes, 70–90 and 80–100 nm, respectively. In the case of the post-added surfactants, the width of the particle size distribution (PSD) is even larger.

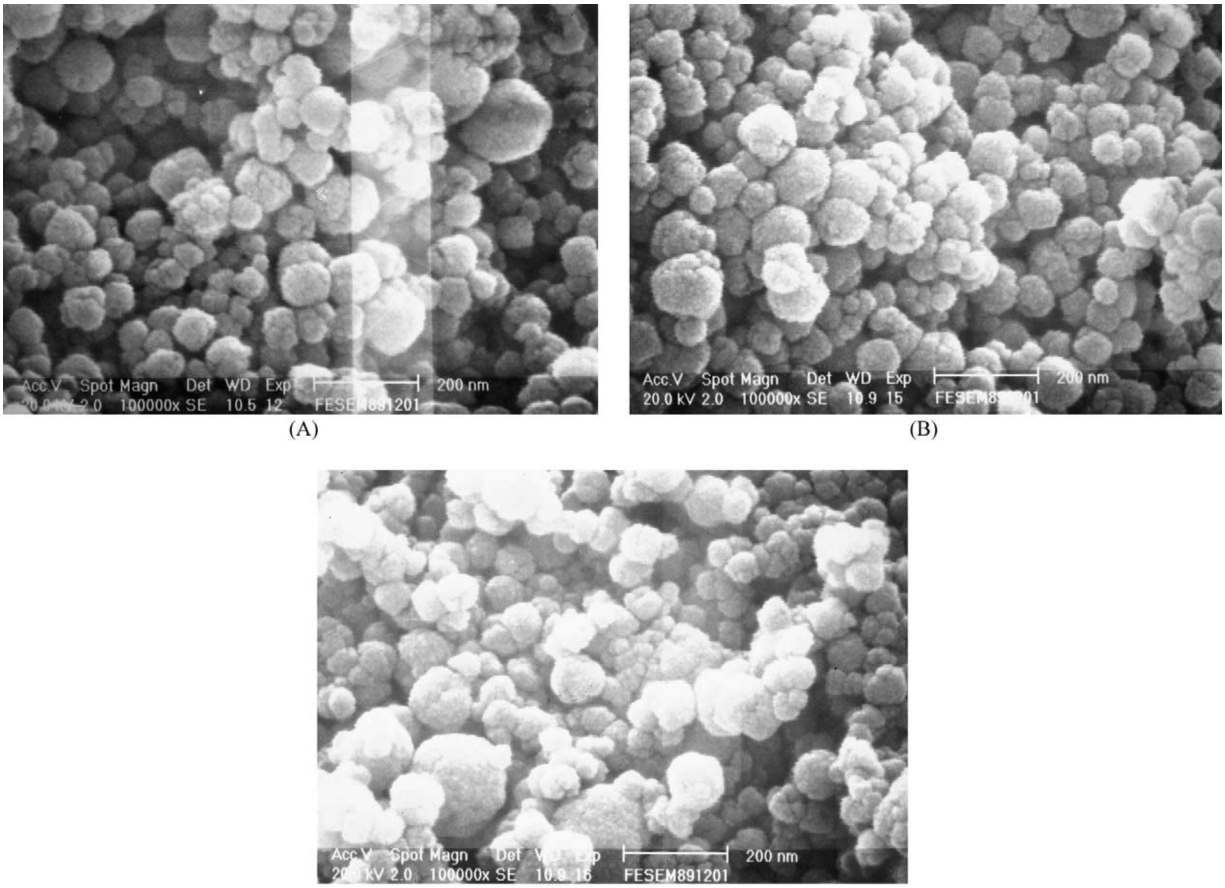
Comparing the pre-added and post-added $BaTiO_3$ powders, all powders obtained with pre-added surfactants were finer than those of the powders with the same surfactant in the post-added process. Especially, the LAS surfactant improved (i.e. made smaller) the particle size effectively; the particle size was about 1/2–3/4 that of the process without a surfactant.

Polar adsorption of Ba^{2+} ions by the formed titanyl acylate precipitate could be responsible for its electroneutrality. The existence of Ba^{2+}, $BaOH^{+}$ and the greater number of OH^{-} counterions on the outside of the titanyl acylate precipitate seem to encourage the initial step of the hydrolysis compared with the lower OH^{-} ion concentration in the titanyl acylate precipitate of this study.

The LAS surfactant, an anionic surfactant, is used in pre-added process to create a micelle,[18] inside which the hydrolysis takes place. It is similar that the reaction of a titanyl acylate precursor in strong alkaline solution the hydrolyzed titanyl acylate gel is formed fast and then becomes $SrTiO_3$, with Sr^{2+} diffusing into the gel.[25] The particle size of the perovskite powders are controlled by the morphology of titanyl acylate formed first. Thus, the precursor precipitate formed through the LAS surfactant pre-added process contains smaller precipitate particles, and the final perovskite powder is also finer.

A large difference in particle size can be attributed to the simultaneous processes of crystal growth and nucleation. But the particle size distribution of the powders may be homogenized by using pre-added surfactants.

Inspection of the data of Table 1 (after calculation of the equivalent BET particle diameter, d_{BET}) and of the SEM micrographs of Figs. 4 and 5 shows that: (1) particles are generally formed by tight agglomerates of nanosized $BaTiO_3$ crystals; (2) the smallest particles



(A)

(B)

(C)

Fig. 5. SEM analysis of the nanometer-sized $BaTiO_3$ powder obtained through post-added surfactant: (A) BKC surfactant added, (B) Tween-20 added, and (C) LAS surfactant added.

visible in Figs. 4 and 5 correspond to the primary $BaTiO_3$ crystallites; (3) aggregation of crystallites, in addition to nucleation and growth of crystallites, is of fundamental importance in determining the PSD of final powder; (4) the adsorption of post-added surfactant molecules at the surface of crystallites influences the agglomeration process and, in particular, leads to bigger particles; (5) the surfactant (in particular LAS) has also an effect on nucleation and growth of the nanosized crystallites. However, even if the surfactant lead to the formation of smaller nanocrystals, the agglomeration process is also promoted. This can be seen by calculating the ratio (mean particle size obtained by SEM)/d_{BED}.

3.2.2. XRD analysis

The XRD pattern of the $BaTiO_3$ powders [powders (S1), (S2), (S3), and (S4)] obtained from the pre-added surfactant process are shown in Fig. 6. Fig. 6(A) shows the XRD pattern of the powder obtained without any surfactant added. It reveals that the powder was consisted of a main perovskite phase and few secondary phases of Magnéli phases (Ti_3O_5, Ti_4O_7 and Ti_5O_9 etc.). Considering that the X-ray scattering factor of Ba is much larger than that of Ti, this probably corresponds to some% of secondary phases. Fig. 6(B) shows the XRD pattern of the product where BKC (a cationic surfactant) was added before precipitation. It is obviously found that the Magnéli phases were also clearly visible as presented in Fig. 6(A).

The perovskite phase in Fig. 6(C) and (D) seems to be more clearly defined than in Fig. 6(A) and (B), meaning that the perovskite formation rate in the anionic or nonionic surfactant is higher than in the cationic surfactant or without any surfactant added. Especially, the powder prepared from the pre-added LAS process shows a strongest perovskite phase and without visible secondary phases [Fig. 6(D)].

By the evidence of SEM, the titanyl acylate precipitate made from pre-added LAS process contains a smaller particle size of powder. Furthermore, it has been shown that hydrolyzed titanyl acylate precursor precipitates in a strong alkaline solution, and that it then reacts with Ba^{2+}, diffused into the precipitate to form $BaTiO_3$.

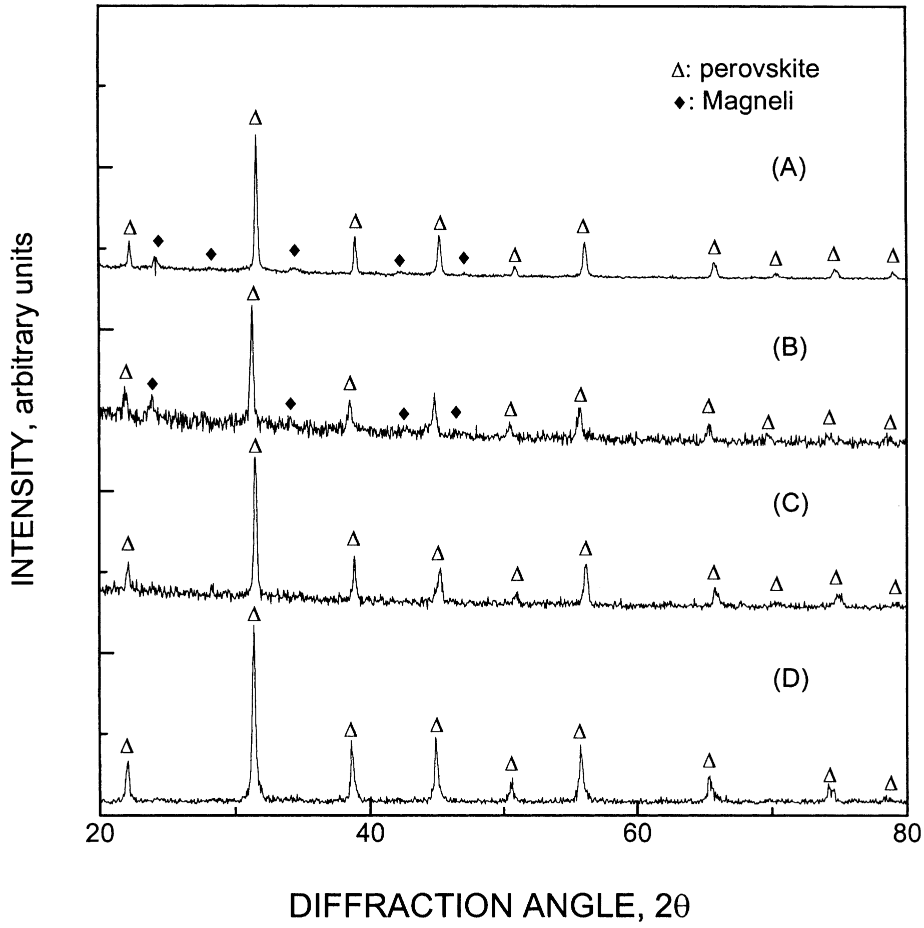


Fig. 6. The XRD patterns of $BaTiO_3$ powder obtained through pre-added surfactant: (A) without any surfactant added, (B) BKC surfactant added, (C) Tween-20 added, and (D) LAS surfactant added.

Hence, this can be explained that the finer particle of the precipitate formed in the pre-added LAS process causes the more rapid formation of $BaTiO_3$ phase, having a strong crystal phase of perovskite and without visible secondary phases.

3.2.3. Measurement of specific surface area

The specific surface areas of the $BaTiO_3$ powders obtained through addition of various surfactants (cationic, anionic and nonionic surfactant) were measured by BET method. The results are listed in Table 1. Aggregation was less if a surfactant was added hence the specific surfaces in the cases were bigger. The specific surface area measured for the powder without any surfactant was small, and agglomeration and particle size large. The specific surface area of $BaTiO_3$ was largest for the LAS pre-added process, it was 60.9 m^2/g. The specific surface area investigation supports the results of the SEM micrographs. After calcination of the equivalent BET particle diameter, it can be inferred that most of particles of Figs. 4 and 5 are composed of smaller primary crystallites.

3.2.4. Sinterability

The calcined powders (S1), (S2), (S3) and (S4) were compacted in a steel die at 110 MPa to obtain green bodies of 13 mm in diameter and 50–55% of pyrometer density. Fig. 7 shows the sintering curves of the four ceramics. Dilatometric curves recorded from the disc specimen clearly indicate that sintering took place between 1200 and 1300 °C for bulk (S1) (made without any surfactant added, largest particle sizes) (Fig. 7). After sintering at 1300 °C for 2 h the specimen reached a density of 96% of its theoretical value. Powder (S4) made from pre-added LAS surfactant powder sintered at 1100–1200 °C, and reached 98% of its theoretical density value at 1250 °C. The powder made from the Tween-20 and BKC surfactants had a particle size of 60–110 nm and 50–130 nm sintered at 1150–1250 °C and 1175–1275 °C, respectively. The above measurements indicate a rela-

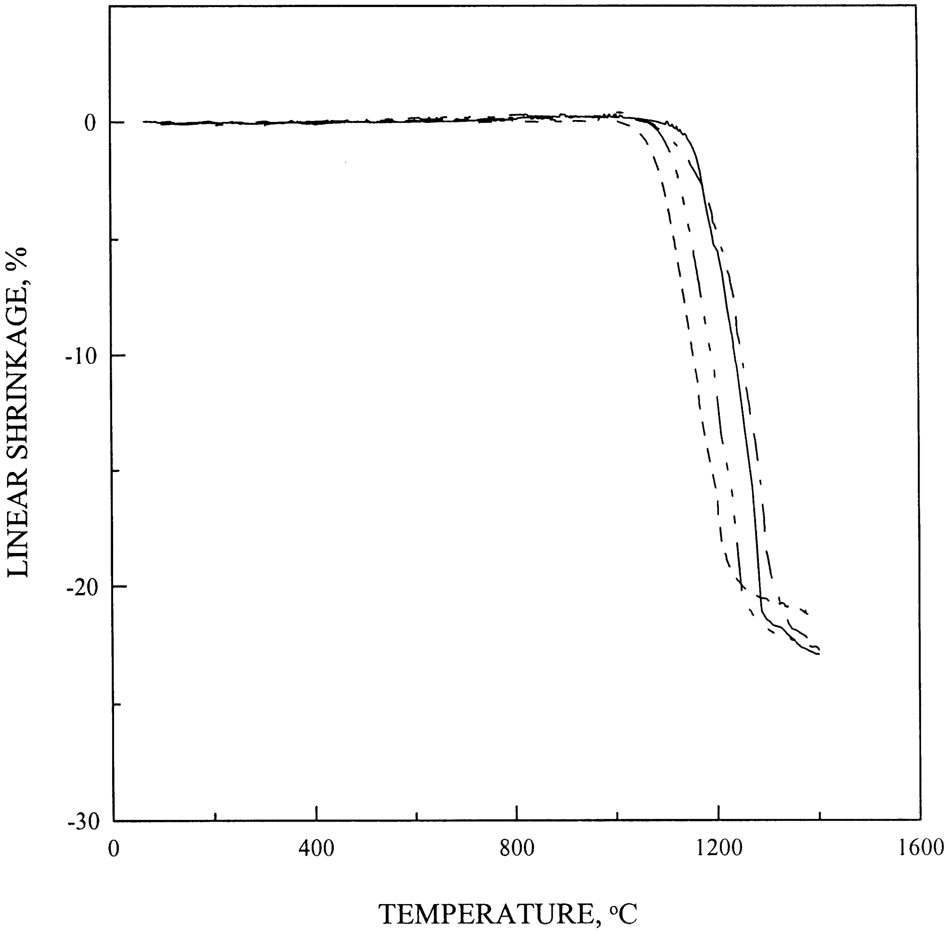


Fig. 7. Dilatometric curves of the packed $BaTiO_3$ samples from various precursors through pre-added surfactant. – – -, Without any surfactant added [sample (S1)], —, BKC surfactant added [sample (S2)], - - - -, Tween-20 added [sample (S3)], and - - - -, LAS surfactant added [sample (S4)].

tionship between the particle size of the powder and its sinterability: the smaller the particles, the more readily the powder sinters.

4. Conclusions

Surfactants were added to titanium isopropoxide with acetic acid as a chemical additive in a strong alkaline solution to precipitate an acylate precursor. This precipitate reacts directly with Ba^{2+} to yield a nanometer-size $BaTiO_3$ powder. By controlling the formation rate of the titanium isopropoxide gel, powders with small particles sizes were obtained. FTIR, TGA and XRD techniques were used to study the influence of the morphology of the precipitated precursors on the powder properties and the sintering behavior of the ceramics. Results show that the particle size of the ceramic powder is related to the morphology of the titanyl acylate precipitate.

The addition of the cationic surfactant LAS before precipitation results in a higher concentration of chelate bidentate ligands, the formation of micelles and a localized OH^- resulting a less crosslinked network structure of smaller particles. However, pre-added BKC anionic surfactant cannot create micelles, and therefore doesn't improve the suspension effectively. Powders obtained with LAS surfactant added had particle sizes of 30–90 nm, and sintered readily at 1100–1200 °C.

Acknowledgements

The authors thank the National Science Council, NSC 90-2626-E-151-001, for the financial support of this work.

References

1. Chan, N. H. and Smyth, D. M., Defect chemistry of $BaTiO_3$. *J. Electrochem. Soc.*, 1976, **123**(10), 1584–1585.
2. Heywang, W., Barium titanate as a semiconductor or with blocking layers. *Solid State Electr.*, 1961, **3**(1), 51–58.
3. Ikegami, S. and Uda, I., Semiconducting single crystal of $BaTiO_3$ reduced in hydrogen atmosphere. *J. Phys. Soc. Jpn.*, 1964, **19**(2), 159–166.

4. Kutty, T. R. N. and Devi, L. G., Photoelectrochemical properties of donor doped $BaTiO_3$ electrodes. *Mater. Res. Bull.*, 1985, **20**, 793–801.
5. Shrout, T. R. and Dougherty, J. P., Lead based $Pb(B_1B_2)O_3$ relaxors vs $BaTiO_3$ dielectrics for multilayer capacitors. *Ceramic Transaction*, 1990, **8**, 3–19.
6. Nemoto, H. and Oda, I., Direct examinations of PTC action of single grain boundaries in semiconducting $BaTiO_3$-ceramics. *J. Am. Ceram. Soc.*, 1980, **63**(7-8), 398–401.
7. Rawal, B. S., Kahn, M. and Buessem, W. R., Grain core–grain shell structure in barium titanate-based dielectrics. In *Advances in Ceramics*, Vol. 1, ed. I. M. Levinson, The American Ceramic Society, 1981, pp. 172–188.
8. Chiou, B. S., Lin, S. T. and Duh, J. G., The effect of sintering conditions on the grain growth of the $BaTiO_3$-based GBBL capacitors. *J. Mater. Sci.*, 1988, **23**, 3889–3893.
9. Uchino, K., Multilayered devices of ferroelectric ceramics. *Mater. Sci. Forum*, 1990, **62**(64), 251–268.
10. Hennings, D., Rosentein, G. and Schreinemacher, H., Hydrothermal preparation of barium titanate from barium-titanium acetate gel precursors. *Journal of the European Ceramic Society*, 1991, **8**, 107–115.
11. Mosset, A., Gautier-Luneau, I. and Galy, J., Sol-gel processed $BaTiO_3$: structural evolution from the gel to the crystalline powder. *J. Non-Cryst. Sol.*, 1988, **100**, 339–344.
12. Moon, J., Suvaci, E., Li, T., Costantino, A. and Adair, J. H., Phase development of barium titanate from chemically modified-amorphous titanium (hydrous) oxide precursor. *J. Eur. Ceram. Soc.*, 2002, **22**, 809–815.
13. Samuneva, B., Jambazov, D., Lepkova, D. and Dimitriev, Y., Sol-gel synthesis of $BaTiO_3$ and $Ba_{1-x-y}Ca_ySr_x(Zr_yTi_{1-y})O_3$ perovskite powders. *Ceram. Int.*, 1990, **16**, 355–360.
14. Wilson, J. M. and Coller, D. L., *Method of Precipitating Metal Titanate Powders*. US Patent, 4,670,243, 2 June 1987.
15. Kao, C. F. and Yang, W. D., Preparation and electrical properties of fine strontium titanate powder from alkoxide in a strong alkaline solution. *Mater. Sci. Eng.*, 1996, **B38**, 127–137.
16. Li, C. C. and Jean, J. H., Interaction of organic additives with boric oxide in aqueous barium titanate suspensions. *J. Am. Ceram. Soc.*, 2002, **85**(6), 1441–1448.
17. Jean, J. H. and Wang, H. R., Stabilization of aqueous $BaTiO_3$ suspensions with ammonium salt of poly(acrylic acid) at various pH values. *J. Mater. Res.*, 1998, **13**(8), 2245–2250.
18. Kiss, K., Magder, J., Vukasovich, M. S. and Lockhart, R. J., Ferroelectrics of ultrafine particle size: I, synthesis of titanate powders of ultrafine particle size. *J. Am. Ceram. Soc.*, 1966, **59**(6), 291–295.
19. Potdar, H. S., Deshpande, S. B., Sainkar, S. R., Mitra, A. and Date, S. K., Use of SDS surfactant in the synthesis of highly dispersed $BaTiO_3$ powders. *Ind. J. Chem. Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 1998, **37**(8), 674–677.
20. Xu, J., Pan, Q., Shun, Y. and Tian, Z., Grain size control gas sensing properties of ZnO gas sensor. *Sensors and Actuators*, 2000, **B66**, 277–279.
21. Phule, P. P. and Risbud, S. H., Sol-gel synthesis of barium titanate powders using barium acetate and titanium isopropoxide. *Adv. Ceram. Mater.*, 1988, **3**, 183–185.
22. Doeuff, S., Henry, M., Sanchez, C. and Livage, J., Hydrolysis of titanium alkoxides: modification of the molecular precursor by acetic acid. *J. Non-Cryst. Sol.*, 1987, **89**, 206–216.
23. Phule, P. P. and Risbud, S. H., Low temperature synthesis and dielectric properties of ceramics derived from amorphous barium titanate gels and crystalline powders. *Mater. Sci. Eng.*, 1989, **B3**, 241–247.
24. Livage, J., Sanchez, C., Henry, M. and Doeuff, S., The chemistry of the sol-gel process. *Sol. State Chem.*, 1989, **32/33**, 633–638.
25. Yang, W. D., Alkyl groups effect on the formation of ultrafine Nb_2O_5-doped $SrTiO_3$ powders by sol-precipitation process. *Mater. Sci. Eng.*, 1999, **A262**, 148–158.