TECHNICAL REPORT

Effect of hydrothermal temperature on the tetragonality of BaTiO₃ nanoparticles and in-situ Raman spectroscopy under tetragonal–cubic transformationHiromichi HAYASHI^{1,†} and Takeo EBINA¹¹Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST), 4–2–1 Nigatake, Miyagino-ku, Sendai 983–8551, Japan

Highly crystalline BaTiO₃ particles were hydrothermally synthesized at 250–400°C from the reactants of TiO₂ sol and Ba(OH)₂ solution. X-ray diffraction measurement patterns revealed that the crystal phase of the obtained particles was tetragonal, whereas tetragonality (*c/a*) was difficult to estimate due to the peak broadening of BaTiO₃ nanoparticles. The particle sizes determined based on the BET surface area and crystallite sizes were almost constant at 80 and 40 nm, irrespective of the hydrothermal temperature. Based on TG–DTA analyses, the lattice OH content decreased with increases in the hydrothermal temperature. In-situ Raman spectra were conducted in the temperature range from 25 to 200°C to follow the tetragonal-to-cubic transformation. The tetragonal-to-cubic phase transition was clearly observed at 120–130°C for the BaTiO₃ hydrothermally synthesized at 400°C, whereas the BaTiO₃ hydrothermally synthesized at 250–350°C exhibited a delayed transition at above 150°C due to pseudo-cubic behavior. The tetragonality of BaTiO₃ synthesized at 400°C can be assumed to be prominent owing to the lower number of lattice OH groups.

©2018 The Ceramic Society of Japan. All rights reserved.

Key-words : Crystal growth, Raman spectroscopy and scattering, Ferroelectricity

[Received June 5, 2017; Accepted January 10, 2018]

1. Introduction

BaTiO₃ has been extensively studied for use as ferroelectric materials in electro-ceramics and utilized in various fields, including multilayer ceramic capacitors (MLCC),^{1)–3)} positive temperature coefficient of resistance thermistors,⁴⁾ electro-optic devices,⁵⁾ and others. The large capacity and device miniaturization of current MLCC requires that the dielectric layer be less than 0.5 μm. Synthesis of uniform BaTiO₃ nanoparticles is essential for the production of thinner dielectric green sheets. Traditionally, BaTiO₃ has been produced via the solid-state reaction,⁶⁾ citrate,^{7),8)} sol–gel,^{9),10)} and hydrothermal method.^{11)–18)}

The hydrothermal method provides fine, monodispersed particles suitable for production of thin dielectric layers, whereas its crystallographic features are cubic rather than tetragonal as a result of lattice defects due to the OH groups incorporated in the perovskite lattice.¹⁹⁾ An alternative supercritical hydrothermal process has been noted that exhibits advantages in terms of rapid kinetics and high supersaturation as compared to the conventional hydrothermal method. The lower dielectric constant of supercritical water is appropriate for promoting the nucleation

and crystal growth of metal oxides, as a result of which rapid hydrothermal synthesis of metal oxides can be achieved in extremely short reaction times.^{20)–25)} In addition, dehydration proceeds at a lower water density under supercritical conditions, producing fewer defective BaTiO₃ nanoparticles as a result.²³⁾

Perovskite BaTiO₃ undergoes a tetragonal-to-cubic phase transition at about the Curie point at around 130°C. The tetragonal phase is a thermodynamically stable phase at room temperature. The pseudo-cubic BaTiO₃ phase formed by hydrothermal synthesis can be stabilized with strains from defects of BaTiO₃ nanoparticles, however, primarily in the form of lattice OH[–] ions and their compensation by cation vacancies. Various researchers assigned BaTiO₃ nanoparticles to the cubic phase based on their X-ray diffraction measurement (XRD) and differential scanning calorimetry results.^{19),26)–31)} Clark et al. argued, by contrast, that the BaTiO₃ nanoparticles are tetragonal rather than cubic according to the presence of Raman-active modes for the tetragonal phase.¹¹⁾

As concerns the correlation between room-temperature tetragonality and the Curie point of BaTiO₃, the Curie point of fine BaTiO₃ powders appeared to increase as the room-temperature tetragonality decreased, as deduced from Raman spectroscopy by Begg.²⁸⁾ We also reported the size effect of BaTiO₃ particles on the in-situ Raman

[†] Corresponding author: H. Hayashi; E-mail: h-hayashi@aist.go.jp

spectra for the tetragonal–cubic transformation in which the intensity at 305 cm^{-1} increased with the temperature and attained a maximum corresponding to the Curie point of BaTiO_3 . The Curie point tended to increase with decreases in the particle size of the BaTiO_3 .³²⁾

In this study, hydrothermal synthesis of BaTiO_3 was conducted by batch reaction with variation of the reaction temperature. The reaction temperature dependence on the crystal phase, particle size and hydroxyl content of the products was discussed with a view to designing a reaction system that allows the synthesis of ferroelectric BaTiO_3 nanoparticles dependent on the dielectric performance of sintered BaTiO_3 ceramics. In addition, in-situ Raman spectra were measured for the hydrothermally synthesized BaTiO_3 to confirm the relationship between the tetragonality and Curie temperature for the tetragonal-to-cubic transformation.

2. Experimental

2.1 Materials

Titanium dioxide sols (Ishihara Techno Corp; STS100: TiO_2 20 wt %, crystallite size 5 nm, pH 1.4 (1.5% HNO_3), and barium hydroxide [$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$; Wako Pure Chemicals Co., Ltd.] were used as starting materials without further purification. Commercial BaTiO_3 powder was purchased from Aldrich Co., Ltd. (nanosized powder: 30–50 nm) as the reference for the hydrothermally synthesized sample.

2.2 Hydrothermal synthesis of BaTiO_3 nanoparticles

BaTiO_3 particles were synthesized at $250\text{--}400^\circ\text{C}$ at a heating rate of 2 K/min to the reaction temperature and a reaction time of 20 min, and cooled naturally by batch-wise operation. Hydrothermal synthesis was carried out using an autoclave-type reactor made from Inconel 625 (Ni–Cr alloys), with an inner volume of 500 cm^3 . A TiO_2 -sol (20 g) was added to a $\text{Ba}(\text{OH})_2$ solution (230 g) and stirred until it became white slurry [0.2 M TiO_2 , $0.24\text{ M Ba}(\text{OH})_2$]. The slurry was entered into a gold-tube container inside the autoclave. Hydrothermal synthesis was carried out at 250 , 300 , 350 and 400°C with autogenous pressures of 2.0 , 2.8 , 5.4 , and 29.1 MPa , respectively. After the reaction and cooling, the autoclave was opened to recover the product particles as a slurry solution, separated with a membrane filter (pore size $0.2\text{ }\mu\text{m}$), washed with 1 M acetic acid solution and deionized water, and finally dried at 60°C in an electric oven for 24 h.

2.3 Measurements

The particle size and the morphology of the obtained particles were examined by transmission electron microscopy (TEM; FEI Co., Model TECNAI-G2) at 200 kV . The crystal structure of the products was determined by XRD (XRD; Rigaku Co., Ltd., Model RINT 2000) using $\text{Cu K}\alpha$ ($\lambda = 1.5418$) radiation. The crystallite sizes were calculated from the peak broadening of the peak (110) for the

tetragonal phase according to the Scherrer equation, $L(110) = 0.9\lambda/\beta\cos\theta$, where λ is the X-ray wavelength used and β is the half-width. The BET surface area of the powder samples was measured by nitrogen adsorption measurement (QUANTACHROME Co., CHEMBET 3000). The calculation of the mean particle size [D] from the BET surface area is described in the equation $D = 6000/s\rho$, where s is the BET surface area [m^2/g] and ρ is the density of BaTiO_3 [6.2 g cm^{-3}] using the crystal lattice density in JCPDS file 31-174. Thermogravimetric analysis was performed using a Bruker thermogravimetry-differential thermal analysis (TG–DTA) simultaneous thermal analyzer (model 2000SA) at a heating rate of 10 K/min to determine the adsorbed water and hydroxyl contents of as-prepared powders. Raman spectroscopy measurement was carried out on a JASCO model NRS-3100 using a 100 mW laser with a wavelength of 532 nm equipped with a heating stage (Japan Hightech Co., Ltd. model 10033). The temperature was changed from 20 to 200°C using a step function, i. e., the temperature was increased at a rate of 5 K/min and, after keeping the temperature constant for 30 min at various temperatures, the Raman spectra were measured. Each spectrum, measured using 180° back-scattered geometry and laser power of 0.8 W , was an average of $60\text{ s} \times 4$ scans, with a nominal resolution of 1 cm^{-1} . For measuring the dielectric properties of BaTiO_3 ceramics, the hydrothermally synthesized powders (3.5 g) were uniaxially pressed at 20 MPa in a steel die to form pellets measuring 20 mm in diameter and $3\text{--}4\text{ mm}$ in thickness, followed by sintering at 1200°C for 5 h. The densities of the sintered specimen were measured by the Archimedes method. The relative density was ca. $92\text{--}95\%$ of the BaTiO_3 crystal lattice density. The dielectric constants and $\tan\delta$ were determined using an Agilent E4980A precision LCR meter at 1 kHz , 1 V and room temperature.

3. Results and discussion

3.1 Characterization of hydrothermally synthesized BaTiO_3 particles

TEM images of the BaTiO_3 particles hydrothermally synthesized at (a) 250 , (b) 300 , (c) 350 , and (d) 400°C for 20 min are shown in **Fig. 1**. BaTiO_3 particles hydrothermally synthesized at 250°C have a round cubic shape with uniform particle size distribution of $50\text{--}100\text{ nm}$. In contrast, BaTiO_3 particles hydrothermally synthesized at 300 and 350°C exhibit wide particle size distribution in the range from 50 nm to 200 nm . BaTiO_3 particles hydrothermally synthesized at 400°C have an average particle size of around 100 nm with uniform particle size distribution.

The reaction of $\text{Ba}(\text{OH})_2$ with TiO_2 can be expressed as follows:

In a homogeneous dissolution–precipitation model, a low concentration of TiO_2 dissolves in the form of soluble hydroxyl titanium complexes which react with Ba^{2+} ions in solution to precipitate BaTiO_3 .¹⁷⁾ The growth

of hydrothermal BaTiO₃ is generally enhanced in a strongly alkaline solution. From a thermodynamic viewpoint, the crystal growth rate increases with increases in the concentration of OH[−], since the solubility of Ti(OH)₅[−] increases at a pH of 11 or higher.²⁰⁾ The single phase of BaTiO₃ can be obtained under high pH conditions, where the dissolution-recrystallization process is essential for the BaTiO₃ synthesis.

Figure 2 shows the XRD patterns of the BaTiO₃ powders hydrothermally synthesized at (a) 250, (b) 300, (c) 350, and (d) 400°C for 20 min using TiO₂ sol and Ba(OH)₂

Fig. 1. TEM images of BaTiO₃ particles synthesized by hydrothermal reaction for a reaction time of 20 min at (a) 250, (b) 300, (c) 350 and (d) 400°C. Scale bar: 100 nm.

solution as starting materials. In the insert, peaks of (111) around $2\theta = 38^\circ$, (002) and (200) around $2\theta = 45.5^\circ$ are enlarged. Each diffraction peak of the particles prepared for this report was assigned to BaTiO₃ (JCPDS 31-174). The peak split at around $2\theta = 45.5^\circ$ is a characteristic indication of the tetragonal BaTiO₃ phase. Although the peak splits were not distinct except in the sample synthesized at 400°C, as-synthesized BaTiO₃ samples can be assigned to the tetragonal phase. This is supported by the full-width half maximum (FWHM) peak ratio of (111)/(200), which value was 0.47–0.57 in **Table 1**.

In the case of cubic BaTiO₃, the FWHM peak ratio of (111)/(200) was 0.93.³²⁾ In the case of tetragonal BaTiO₃, FWHM (200) was larger than FWHM (111) since peak (200) overlapped with (002) without showing clear peak splitting. The tetragonality of BaTiO₃ nanoparticles, however, can not be readily estimated using X-ray powder diffractometry.

The BET surface area and average particle sizes of BaTiO₃ calculated by means of the BET surface area of the particles are also shown in Table 1 together with the average particle sizes estimated from TEM observation and the crystallite sizes estimated from the (110) diffraction peak width. The average particle sizes of BaTiO₃ appeared somewhat larger than the crystallite sizes of BaTiO₃, presumably due to the discrepancy between the density of BaTiO₃ particles and the crystal lattice density, whereas the trend of the order of average particle sizes was consistent with that of the crystallite sizes. Consequently, the average particle sizes and crystallite sizes of the BaTiO₃ powders were not significantly different, irrespective of hydrothermal temperatures.

The weight loss amounts for the BaTiO₃ in the temperature range up to 600°C are summarized in Table 1. The

Fig. 2. XRD profiles of BaTiO₃ particles synthesized by hydrothermal reaction for a reaction time of 20 min at (a) 250, (b) 300, (c) 350 and (d) 400°C.

Table 1. Characterization of BaTiO₃ nanoparticles

Sample	AP ^{a)} (nm)	SSA ^{b)} (m ² /g)	D ^{c)} (nm)	L ^{d)} (nm)	a ^{d)} (Å)	c/a ^{d)}	FWHM ratio ^{e)}	WL ^{f)} (wt %)	ε ^{g)}	tan δ ^{g)}
HT250	69.8	12.3	78.7	39.1	4.014	1.000	0.574	1.11	4030	0.067
HT300	88.0	11.9	81.3	38.7	4.010	1.000	0.529	0.45	3430	0.224
HT350	106.7	10.5	91.8	39.2	4.024	1.000	0.473	0.43	3650	0.336
HT400	119.0	10.5	92.5	40.8	3.997	1.007	0.499	0.17	4550	0.711
Aldrich	66.1	13.0	74.5	30.9	4.019	1.000	0.685	1.96	—	—

^{a)} AP (Average particle size): estimated from TEM observation. ^{b)} SSA (specific surface area): measured by nitrogen adsorption isotherms using the BET equation. ^{c)} Calculated from the BET surface area using the following equation: $D = 6000/s\rho$, where s is the BET surface area [m²/g] and ρ is the density of BaTiO₃ [6.2 g/cm³]. ^{d)} Calculated from the XRD diffraction peak (110) of BaTiO₃ using the Scherer equation. $L(110) = 0.9\lambda/\beta\cos\theta$, where λ is the X-ray wavelength used and β is the half-width. ^{e)} Calculated from the FWHM of XRD diffraction peaks (111) and (200) of BaTiO₃. ^{f)} WL (weight loss): measured by the TG-DTA technique in the temperature range of 200–600°C. ^{g)} Measured pellet samples using an Agilent E4980A precision LCR meter at 1 kHz, 1 V and room temperature. The pellets were sintered at 1200°C.

weight loss up to 200°C is presumably due to the elimination of water adsorbed on the surface, and the weight loss in the 200–600°C range can be attributed to dehydration from the OH[−] incorporated in the lattice. The weight losses up to 600°C were not appreciable amounts and decreased with increases in the hydrothermal temperature. The weight losses (200–600°C) of the BaTiO₃ powders hydrothermally synthesized at 250, 300, 350 and 400°C were 1.11, 0.45, 0.43 and 0.17 wt %, respectively. The commercial BaTiO₃ powder (Aldrich) is similar to the present hydrothermally synthesized BaTiO₃, especially to that synthesized at 250°C.

BaTiO₃ particles require better sintering behaviors and higher dielectric constants for application as MLCC device. The dielectric properties of BaTiO₃ pellets sintered at 1200°C are summarized in Table 1. The dielectric constants are over 3000 and a maximum value of 4550 was obtained for the BaTiO₃ pellets hydrothermally synthesized at 400°C, whereas tan δ increased with the hydrothermal temperature. The dielectric constant of a BaTiO₃ sintered sample hydrothermally synthesized at 250°C was larger than those of BaTiO₃ sintered samples hydrothermally synthesized at 300 and 350°C. SEM images for the BaTiO₃ sintered sample hydrothermally synthesized at 250°C reveal that the grain growth was significant compared to those of the other samples.

3.2 In situ Raman spectra for BaTiO₃ particles on the phase transition

Tetragonality can be confirmed by Raman spectroscopy of the BaTiO₃ powder samples. **Figure 3** shows the room temperature Raman spectra of the hydrothermally synthesized BaTiO₃ powders at (a) 250, (b) 300, (c) 350, and (d) 400°C for 20 min. The bands at around 515 and 260 cm^{−1} are assigned to the transverse optical modes of A₁ symmetry A₁(2TO).³²⁾ Other weak peaks are observed at 185, 463 and 720 cm^{−1}, which can be attributed to the E(2TO) + E(1LO) + A₁(1TO) + A₁(1LO), E(4TO) + A₁(3TO) and A₁(3LO) + E(4LO) modes, respectively.³³⁾ The sharp peak at 305 cm^{−1} is assigned to the B₁ mode + E(3TO) + E(2LO), which is characteristic of the tetragonal BaTiO₃ phase. The spectra for BaTiO₃ particles synthesized at 250 and 300°C are overlapping, and the

Fig. 3. Raman spectra of BaTiO₃ particles synthesized by hydrothermal reaction for a reaction time of 20 min at (a) 250, (b) 300, (c) 350 and (d) 400°C.

peak at 305 cm^{−1} is intensified in sharpness and becomes distinct as the hydrothermal temperature increases from 300 to 400°C. Although the peak area increased with increases in the hydrothermal temperature, the normalized peak intensities estimated from the peak area and peak height of the BaTiO₃ powders hydrothermally synthesized at 250, 300, 350 and 400°C were almost constant at 2.73, 3.16, 3.13 and 2.82, respectively.

Figures 4 and 5 show in-situ Raman spectra of BaTiO₃ particles synthesized by hydrothermal reaction at 250°C (Fig. 4) and 400°C (Fig. 5) with variation of the in-situ temperatures in the range of 25–200°C. First, reversible behavior with respect to the in-situ temperature was confirmed by a cooling process from 200°C to room temperature. This indicated that the temperature dependence of intensity at 305 cm^{−1} is reversible, and no annealing effect was observed when heating the samples up to 200°C. In the case of BaTiO₃ synthesized at 250°C, the peak at 305 cm^{−1} increased with increases in the in-situ temperature and reached the maximum at 150°C, after which it decreased with the in-situ temperature. The peak at 305 cm^{−1} remained, however, even at 170 and 180°C. In the case of BaTiO₃ synthesized at 400°C, the sharpness of the peak at

Fig. 4. In-situ Raman spectra of BaTiO₃ particles synthesized at 250°C. Values represent measurement temperatures (°C).

Fig. 5. In-situ Raman spectra of BaTiO₃ particles synthesized at 400°C. Values represent measurement temperatures (°C).

305 cm^{-1} was reduced as the in-situ temperature increased up to 100°C and became indistinct at $110\text{--}130^\circ\text{C}$. The disappearance between 130 and 140°C of both the sharp band at 305 cm^{-1} and the broader band at 720 cm^{-1} indicates that the tetragonal phase is transformed to the cubic phase. The Raman band at 305 cm^{-1} can thus be used to monitor structural phase transitions in BaTiO₃ particles.^{34)–38)}

To discuss this in more detail, (a) plots of the full-width at half maximum (FWHM), (b) the normalized peak intensity at 305 cm^{-1} , and (c) the Raman shift for the BaTiO₃ particles as a function of in-situ temperature in the range of 25 to 200°C are shown in **Figure 6**. The Raman peak area at 305 cm^{-1} normalized to the intensity at 280 cm^{-1} .³⁹⁾ A drastic peak broadening, Raman shift and sharp drop in the intensity at 305 cm^{-1} was observed at 130°C for BaTiO₃

particles synthesized at 400°C . By contrast, peak broadening, and a Raman shift were observed at above 150°C along with a more gradual decrease in intensity over the entire temperature range for the BaTiO₃ particles synthesized at $250\text{--}350^\circ\text{C}$. The Raman linewidth (FWHM) for the BaTiO₃ particles synthesized at $300\text{--}350^\circ\text{C}$ displayed near the tetragonal-to-cubic phase transition in the temperature range of $120\text{--}150^\circ\text{C}$ is similar to the linewidth displayed by the BaTiO₃ particles synthesized at 400°C due in part to a tetragonal contribution. The Curie temperature (T_C) of BaTiO₃ particles synthesized at 250°C shifted to a higher temperature due to pseudo-cubic behavior. The Curie temperature tends to increase with decreases in the hydrothermal temperature. This trend is in accord with the Raman study of the relationship between room-

Fig. 6. (a) Temperature dependence of full-width at half maximum (FWHM), (b) normalized peak intensity at 305 cm⁻¹, and (c) Raman shift for tetragonal BaTiO₃ particles synthesized by hydrothermal reaction at 250 (○), 300 (△), 350 (□), and 400°C (●). Raman signal normalized to the intensity at 280 cm⁻¹.

temperature tetragonality and the Curie point of barium titanate.⁴⁰⁾ The variable-temperature Raman spectroscopy showed that the Curie point increased as the room temperature tetragonality decreased. As the room-temperature tetragonality decreases, the Raman band at 305 cm⁻¹ is retained at higher temperatures. As mentioned previously, the pseudo-cubic BaTiO₃ phase formed by hydrothermal synthesis can be stabilized with strains from defects in BaTiO₃ nanoparticles, primarily in the form of lattice OH⁻ ions and their compensation by cation vacancies. Since dehydration is promoted more under supercritical conditions than under conventional hydrothermal conditions, lattice hydroxyl groups can be reduced under supercritical conditions.²²⁾

4. Conclusions

Hydrothermal synthesis of BaTiO₃ was conducted with variation of the reaction temperatures in order to control the hydroxyl content of the BaTiO₃ crystal lattice. The particle size and crystallite size of BaTiO₃ were almost constant at ca. 80–90 nm from the BET surface area and 40 nm from the L(110) width, irrespective of the hydrothermal temperature.

Based on TG-DTA analyses, the lattice hydroxyl content decreased with increases in the hydrothermal temperature. Thus, tetragonality might be related to the lattice hydroxyl content as well as to the particle size.

In situ Raman spectroscopy is a useful technique for analyzing the structural phase transition of BaTiO₃ particles from tetragonal to cubic. A tetragonal-to-cubic phase transition was clearly observed at 120–130°C for the BaTiO₃ hydrothermally synthesized at 400°C, whereas the BaTiO₃ hydrothermally synthesized at 250–350°C exhibited a delayed transition at above 150°C due to pseudo-cubic behavior.

Acknowledgement The authors would like to express their gratitude to Dr. Yasushi Hoshi (Iwate University) for his preparation of dielectric BaTiO₃ ceramics and measurement of dielectric properties.

References

- 1) D. F. K. Hennings, C. Metzmaier and B. S. Schreinemacher, *J. Am. Ceram. Soc.*, **84**, 179–182 (2001).
- 2) J.-Y. Lee, S.-H. Hong, J.-H. Lee, Y. K. Lee and J.-Y. Choi, *J. Am. Ceram. Soc.*, **88**, 303–307 (2005).
- 3) S. Mustofa, T. Araki, T. Furusawa, M. Nishida and T. Hino, *Mater. Sci. Eng. B-Adv.*, **103**, 128–134 (2003).
- 4) J. Nowotny and M. Rekas, *Solid State Ionics*, **49**, 135–154 (1991).
- 5) M. S. Zhang, Z. Yin, Q. Chen and W. Chen, *Solid State Commun.*, **119**, 659–663 (2001).
- 6) C.-Y. Chang, C.-Y. Huang, Y.-C. Wu, C.-Y. Su and C.-L. Huang, *J. Alloy. Compd.*, **495**, 108–112 (2010).
- 7) L. A. Perez-Maqueda, M. J. Dianez, F. J. Gotor, M. J. Sayagues, C. Real and J. M. Criado, *J. Mater. Chem.*, **13**, 2234–2241 (2003).
- 8) P. R. Arya, P. Jha and A. K. Ganguli, *J. Mater. Chem.*, **13**, 415–423 (2003).
- 9) Y. Kobayashi, A. Nishikawa, T. Tanase and M. Konno, *J. Sol-Gel Sci. Techn.*, **29**, 49–55 (2004).
- 10) B. A. Hernandez, K.-S. Chang, E. R. Fisher and P. K. Dorhout, *Chem. Mater.*, **14**, 480–482 (2002).
- 11) I. J. Clark, T. Takeuchi, N. Ohtori and D. C. Sinclair, *J. Mater. Chem.*, **9**, 83–91 (1999).
- 12) H. Xu, L. Gao and J. Guo, *J. Eur. Ceram. Soc.*, **22**, 1163–1170 (2002).
- 13) X. Zhu, J. Zhu, S. Zhou, Z. Liu and N. Ming, *J. Cryst. Growth*, **310**, 434–441 (2008).
- 14) X. Wang and B. I. Lee, *J. Mater. Sci.*, **14**, 495–500 (2003).
- 15) A. Testino, M. T. Buscaglia, V. Buscaglia, M. Viviani,

- C. Bottino and P. Nanni, *Chem. Mater.*, **16**, 1536–1543 (2004).
- 16) Y. Xie, S. Yin, T. Hashimoto, Y. Tokano, A. Sasaki and T. Sato, *J. Eur. Ceram. Soc.*, **30**, 699–704 (2010).
- 17) J. O. Eckert, C. C. Hung-Houston, B. I. Gersten, M. M. Lencka and R. Riman, *J. Am. Ceram. Soc.*, **79**, 2929–2939 (1996).
- 18) W. Sun, Y. Pang, J. Li and W. Ao, *Chem. Mater.*, **19**, 1772–1779 (2007).
- 19) T. Noma, S. Wada, M. Yano and T. Suzuki, *J. Appl. Phys.*, **80**, 5223–5233 (1996).
- 20) H. Reveron, C. Aymonier, A. Loppinet-Serani, C. Elissalde, M. Maglione and F. Cansell, *Nanotechnology*, **16**, 1137–1143 (2005).
- 21) M. Atashfaraz, M. Shariaty-Niassar, S. Ohara, K. Minami, M. Umetsu, T. Naka and T. Adschiri, *Fluid Phase Equilib.*, **257**, 233–237 (2007).
- 22) Y. Hakuta, H. Ura, H. Hayashi and K. Arai, *Mater. Lett.*, **59**, 1387–1390 (2005).
- 23) Y. Hakuta, H. Ura, H. Hayashi and K. Arai, *Ind. Eng. Chem. Res.*, **44**, 840–846 (2005).
- 24) K. Matsui, T. Noguchi, N. M. Islam, Y. Hakuta and H. Hayashi, *J. Cryst. Growth*, **310**, 2584–2589 (2008).
- 25) H. Hayashi, T. Noguchi, N. M. Islam, Y. Hakuta, Y. Imai and N. Ueno, *J. Cryst. Growth*, **312**, 1968–1972 (2010).
- 26) M. Wu, J. Long, G. Wang, A. Huang and Y. J. Luo, *J. Am. Ceram. Soc.*, **82**, 3254–3256 (1999).
- 27) S. W. Lu, B. I. Lee, Z. L. Wang and W. D. Samuels, *J. Cryst. Growth*, **219**, 269–276 (2000).
- 28) B. D. Begg, E. R. Vance and J. Nowotny, *J. Am. Ceram. Soc.*, **77**, 3186–3192 (1994).
- 29) P. K. Dutta and J. R. Gregg, *Chem. Mater.*, **4**, 843–846 (1992).
- 30) M. Boulos, S. G-Fritsch, F. Mathieu, B. Durand, T. Lebey and V. Bley, *Solid State Ionics*, **176**, 1301–1309 (2005).
- 31) H.-J. Chen and Y.-W. Chen, *Ind. Eng. Chem. Res.*, **42**, 473–483 (2003).
- 32) H. Hayashi, T. Nakamura and T. Ebina, *J. Phys. Chem. Solids*, **74**, 957–962 (2013).
- 33) G. Busca, V. Buscaglia, M. Leoni and P. Nanni, *Chem. Mater.*, **6**, 955–961 (1994).
- 34) B. D. Begg, K. S. Finnie and E. R. Vance, *J. Am. Ceram. Soc.*, **79**, 2666–2672 (1996).
- 35) S. Wada, T. Suzuki, M. Osada, M. Kakihana and T. Noma, *Jpn. J. Appl. Phys.*, **37**, 5385–5393 (1998).
- 36) M. E. Marssi, F. L. Marrec, I. A. Lukyanchuk and M. G. Karkut, *J. Appl. Phys.*, **94**, 3307–3312 (2003).
- 37) P. L. Logos, R. Z. Hermans, N. Velasco, G. Tarrach, F. Schlaphof, C. Loppacher and L. M. Eng, *Surf. Sci.*, **532–535**, 493–500 (2003).
- 38) Z. Lazarevic, N. Romcevic, M. Vijatovic, N. Paunovic, M. Romcevic, B. Stojanovic and Z. Dohcevic-mitrovic, *Acta. Phys. Pol. A*, **115**, 808–810 (2009).
- 39) B. D. Begg, K. S. Finnie and E. R. Vance, *J. Am. Ceram. Soc.*, **79**, 2666–2672 (1996).
- 40) M. B. Smith, K. Page, T. Siegrist, P. L. Redmond, E. C. Walter, R. Seshadri, L. E. Brus and M. L. Steigerwald, *J. Am. Ceram. Soc.*, **130**, 6955–6963 (2008).