J Mater Sci (2007) 42:640–645
DOI 10.1007/s10853-006-1142-0

Hydrothermal soft chemical synthesis of $BaTiO_3$ and titanium oxide with cocoon-like particle morphology

**Qi Feng · M. Hirasawa · K. Kajiyoshi ·
K. Yanagisawa**

Received: 27 August 2004 / Accepted: 17 November 2005 / Published online: 21 December 2006

Abstract The hydrothermal reactions of fibrous $H_2Ti_4O_9$ particles with $Ba(OH)_2$ solution in the presence of cationic surfactants of n-hexadecyltrimethylammonium hydroxide (HTMA-OH) and n-hexadecyl trimethylammonium bromide (HTMA-Br) were investigated in a temperature range of 150–250 °C. $H_2Ti_4O_9$ phase with layered structure was transformed to $BaTiO_3$ phase in the $Ba(OH)_2$–(HTMA-OH) and the $Ba(OH)_2$–(HTMA-Br) solutions, and partially transformed to anatase phase in the Ba^{2+}-free HTMA-OH and HTMA-Br solutions by topotactic structural transformation reactions under the hydrothermal conditions. The cocoon-like $BaTiO_3$ and titanium oxide particles were obtained after the hydrothermal reactions in the $Ba(OH)_2$–(HTMA-OH) and HTMA-OH solution, respectively. These cocoon-like particles were formed by assembling the fibrous particles in the surfactant solutions.

Introduction

Barium titanate ($BaTiO_3$) is a well known electroceramic material widely utilized in the manufacture of multilayer capacitors, thermistors, and electro-optic devices due to its high dielectric permittivity and ferroelectric properties [1, 2]. $BaTiO_3$ particles have been prepared by using various methods. High purity $BaTiO_3$ with controlled particle size can be prepared by using the hydrothermal [3–5] and sol–gel methods [6–8]. However, these methods usually give the particles with a spherical or cubic shape, meaning it is difficult to prepare $BaTiO_3$ particles with special shape, such as fibrous and plate-like particles which have potential application in the preparation oriented dielectric ceramics.

Soft chemical synthesis using host-guest reactions is a unique and useful method for inorganic material synthesis. In the soft chemical synthesis, a compound with layered structure or open structure can be used as the precursor. The layered structure of the precursor can be transformed to a desired structure by an in situ topotactic structural transformation reaction, and the morphology of the precursor can be retained after the reaction [9–12]. This means that the morphology of the product is dependent on that of the precursor, which is different from normal methods, e.g. sol–gel method and hydrothermal method, where the crystal particle morphology is almost independent of the morphology of the precursor. Hydrothermal reaction is useful for the structural transformation in the soft chemical synthesis. Fibrous $BaTiO_3$ and $PbTiO_3$ particles have been prepared by hydrothermally reacting a fibrous layered hydrous potassium titanate ($2K_2O{\cdot}11TiO_2{\cdot}3H_2O$) in $Ba(OH)_2$ and $Pb_2O(OH)_2$ solutions, respectively [13–15]. These fibrous $BaTiO_3$ and $PbTiO_3$ particles show high degree crystal-axis orientation and anisotropic dielectric properties. Our previous study has indicated that plate-like and fibrous

---

Q. Feng (✉)
Department of Advanced Materials Science,
Faculty of Engineering, Kagawa University,
2217-20 Hayashi, Takamatsu 761-0396, Japan
e-mail: feng@eng.kagawa-u.ac.jp

M. Hirasawa · K. Kajiyoshi · K. Yanagisawa
Research Laboratory of Hydrothermal Chemistry,
Faculty of Science, Kochi University, 2-5-1 Akebono,
Kochi 780-8520, Japan

anatase and $BaTiO_3$ particles can be prepared by hydrothermally reacting H^+-form layered titanates of $H_{1.07}Ti_{1.73}O_4$ and $H_2Ti_4O_9$ with plate-like and fibrous particle morphologys in distilled water and $Ba(OH)_2$ solution, respectively [16, 17]. The transformation reactions from the layered phase to the anatase and $BaTiO_3$ phases are in situ topotactic reactions. The anatase and $BaTiO_3$ particles prepared by this method also show high degree crystal-axis orientation properties.

In the present paper, we describe preparation of $BaTiO_3$ and titanium oxide from fibrous $H_2Ti_4O_9$ precursor with a layered structure by hydrothermal reaction in the presence of a cationic surfactant. In this reaction system, the fibrous product particles can be assembled, and shaped into cocoon-like particles, which provides a new process for modification of particle morphology in the soft chemical synthesis.

Experiment

Fibrous layered $K_2Ti_4O_9$ (Otsuka Chemical Co., Ltd) with dimensions of 0.3–0.6 μm in diameter and 10–20 μm in length was used as the precursor. The fibrous $K_2Ti_4O_9$ particles (10 g) were treated in a 1 M HNO_3 solution (1 L) for 1 day at room temperature to exchange K^+ in the layered structure with H^+. The acid-treatment was repeated for twice to complete the ion-exchange reaction, and fibrous $H_2Ti_4O_9$ particles were obtained after the ion-exchange reaction. The ion-exchanged sample was washed with distilled water and dried at room temperature.

The fibrous $H_2Ti_4O_9$ (0.147 g) was added into a 0.1 M cationic surfactant solution (15 mL) of n-hexadecyltrimethylammonium hydroxide (HTMA-OH) or n-hexadecyltrimethylammonium bromide (HTMA-Br), and stirred at room temperature for 2 h, and then a desired amount of $Ba(OH)_2 \cdot 8H_2O$ solid was added into the solution to adjust the concentration of $Ba(OH)_2$ to 0, 0.1, 0.2, and 0.3 M, respectively. Thus, the Ba/Ti molar ratios in the reaction system are controlled to be 0, 1, 2, and 3, respectively. The mixture (15 mL) was placed in a Teflon-lined, sealed stainless steel vessel (30 mL of inner volume), and then hydrothermally treated in a temperature range of 150–250 °C for 24 h under autogenously pressure and stirring conditions. The product was filtered, washed with hot distilled water, and then dried at 80 °C for 24 h.

The crystal structures of samples were investigated by using a powder X-ray diffractometer (Rigaku Rotaflex RAD-RC). The particle size and morphology were characterized by scanning electron microscopy (SEM, Hitachi S-530).

Results and discussion

$K_2Ti_4O_9$ has a layered structure with K^+ and water molecules in the interlayer space, and the K^+ are ion-exchangeable [9]. After the acid-treatment, K^+ were exchanged with H^+, but retained the layered structure (Fig. 1a) with a basal spacing of 0.791 nm, and retained its fibrous particle morphology (Fig. 2a). When $H_2Ti_4O_9$ was treated in a 0.1 M $Ba(OH)_2$ solution at room temperature, the basal spacing of the layered

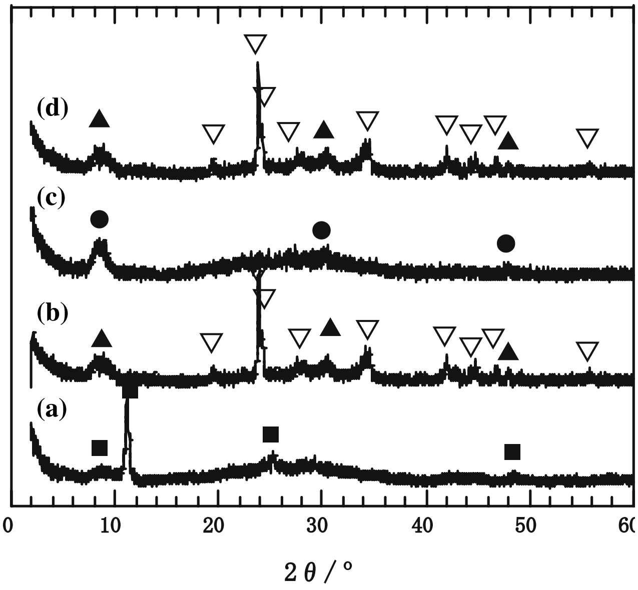

Fig. 1 X-Ray diffraction patterns of (**a**) $H_2Ti_4O_9$ used as the precursor, samples obtained by reacting $H_2Ti_4O_9$ in (**b**) 0.3 M $Ba(OH)_2$ solution and (**c**) 0.1 M HTMA-OH solution, respectively, and (**d**) sample after reacting sample (**c**) in 0.3 M $Ba(OH)_2$ solution, for 1 day at room temperature. ■: $H_2Ti_4O_9$ phase; ▲: Ba^{2+}-exchanged layered phase; ●: $HTMA^+$-exchanged layered phase; ▽: $BaCO_3$ phase

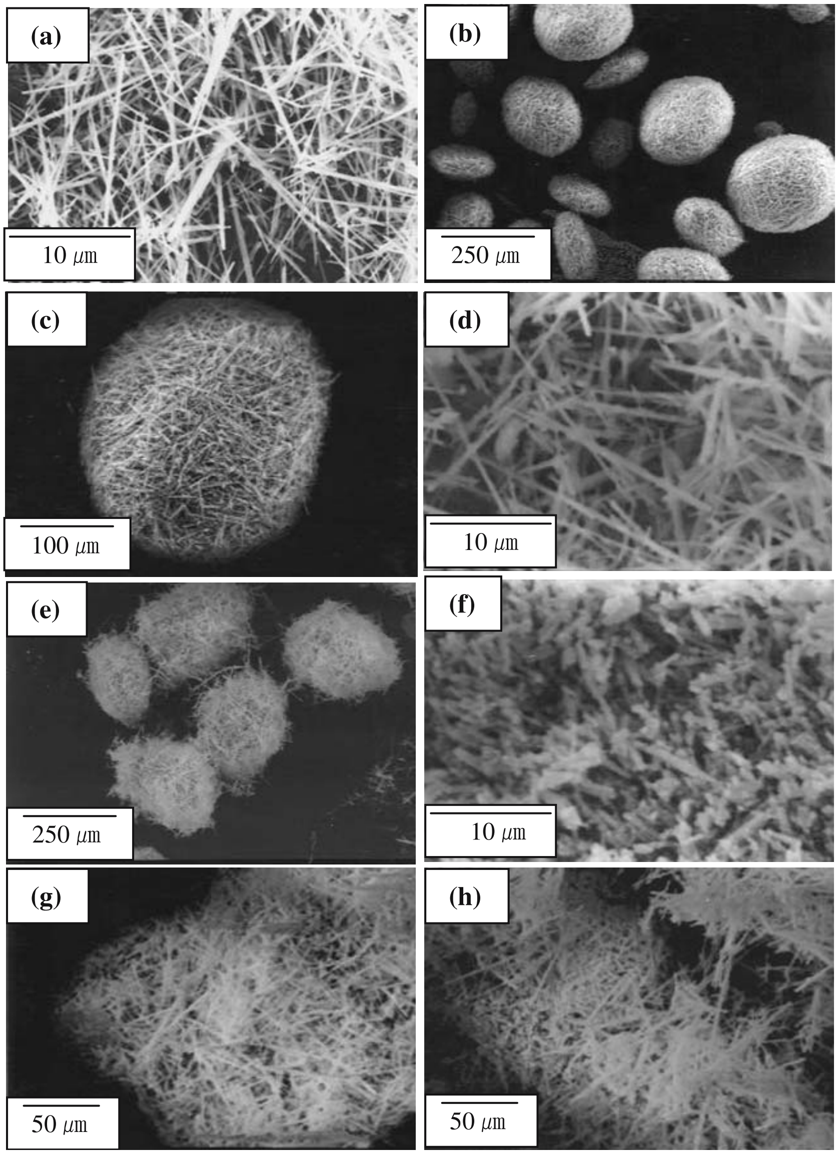

Fig. 2 SEM photographs of (**a**) $H_2Ti_4O_9$ used as the precursor and (**b**)–(**h**) products obtained by hydrothermally reacting $H_2Ti_4O_9$ under stirring conditions for 1 day. (**b**), (**c**) and (**d**) in 0.1 M HTMA-OH solution at 150, 200 and 250 °C, respectively; (**e**) and (**f**) in 0.3 M $Ba(OH)_2$–(HTMA-OH) solution at 150 and 250 °C, respectively; (**g**) and (**h**) in 0.1 M HTMA-Br solution and 0.3 M $Ba(OH)_2$–(HTMA-Br) solution, respectively, at 150 °C

titanate increased from 0.791 to about 1.1 nm (Fig. 1b), indicating that Ba^{2+} can be intercalated into the interlayer space by a Ba^{2+}/H^+ ion-exchange reaction. An impurity phase of $BaCO_3$ was also observed in the sample, due to the reaction of $Ba(OH)_2$ solution and CO_2 gas in air. When $H_2Ti_4O_9$ was treated in HTMA-OH solution at room temperature, the basal spacing of the layered titanate increased from 0.791 to 1.13 nm (Fig. 1c), indicating that $HTMA^+$ can be intercalated into the interlayer space by a $HTMA^+/H^+$ ion-exchange reaction. The $HTMA^+$ in the interlayer space can be exchanged with Ba^{2+}. After treatment of the $HTMA^+$-exchanged layered titanate in $Ba(OH)_2$ solution, product shows a same XRD pattern as that of Ba^{2+}-exchanged titanate (Fig. 1d). The above results reveal that Ba^{2+} can be intercalated easily into the interlayer space of the layered titanate by the ion-exchange reaction, which is important for the soft chemical synthesis of $BaTiO_3$.

Figure 3 shows XRD patterns of samples obtained by hydrothermally reacting $H_2Ti_4O_9$ in $Ba(OH)_2$–(HTMA-OH) solutions at 150 °C under stirring conditions. Most of the layered titanate phase was transformed to a $BaTiO_3$ phase, and only very small amount of unreacted layered titanate phase remained after the reaction in the $Ba(OH)_2$–(HTMA-OH) solution. The amount of unreacted layered titanate phase decreased with increasing the concentration of $Ba(OH)_2$. The layered titanate phase partially transformed to anatase phase in Ba^{2+}-free HTMA-OH solution (Fig. 3a). The formation of $BaTiO_3$ phase increased with increasing the reaction temperature in the $Ba(OH)_2$–

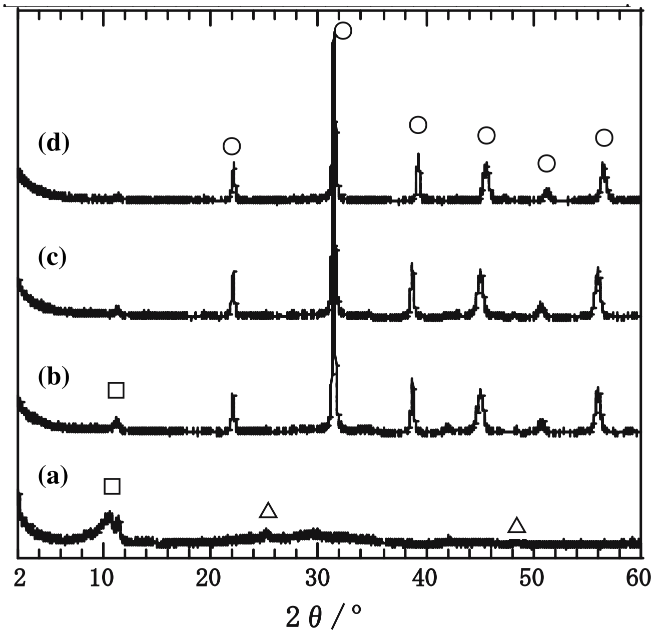

Fig. 3 X-ray diffraction patterns of products obtained by hydrothermally reacting $H_2Ti_4O_9$ in (**a**) 0, (**b**) 0.1, (**c**) 0.2, and (**d**) 0.3 M $Ba(OH)_2$–(HTMA-OH) solutions, respectively, at 150 °C for 1 day under stirring conditions. □: unreacted layered titanate phase; △: anatase phase; ○: $BaTiO_3$ phase

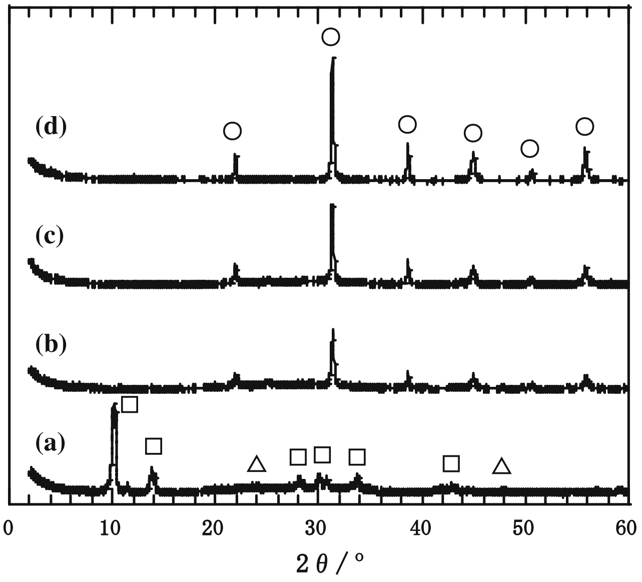

Fig. 4 X-ray diffraction patterns of products obtained by hydrothermally reacting $H_2Ti_4O_9$ in (**a**) 0, (**b**) 0.1, (**c**) 0.2, and (**d**) 0.3 M $Ba(OH)_2$–(HTMA-OH) solutions, respectively, at 250 °C for 1 day under stirring conditions. □: unreacted layered titanate phase;△: anatase phase; ○: $BaTiO_3$ phase

(HTMA-OH) solution. The single $BaTiO_3$ phase was obtained in 0.2 and 0.3 M $Ba(OH)_2$–(HTMA-OH) solutions at 200 °C. At 250 °C the single $BaTiO_3$ phase was obtained in 0.1, 0.2, 0.3 M $Ba(OH)_2$–(HTMA-OH) solutions, but most of the layered titanate phase remained even after reaction at 250 °C in the Ba^{2+}-free HTMA-OH solution (Fig. 4).

The above results indicate that $Ba(OH)_2$–(HTMA-OH) solution shows an almost same reactivity for the formation of $BaTiO_3$ phase as that of $Ba(OH)_2$ solution, while HTMA-OH solution shows a lower reactivity for the formation of the anatase phase than that of distilled water under the hydrothermal conditions [17]. The $BaTiO_3$ phase is formed mainly by an in situ topotactic transformation reaction similar to the case in the $H_2Ti_4O_9$–$Ba(OH)_2$ reaction system, in which Ba^{2+} migrate into the crystal bulk of layered titanate through the interlayer space, and then react with titanate layers to form $BaTiO_3$ in the crystal bulk. The transformation from $H_2Ti_4O_9$ phase to anatase phase is a dehydration reaction. The $H_2Ti_4O_9$ phase can be transformed completely to anatase phase after reaction in distilled water at 200 °C. The XRD results suggest that the $H_2Ti_4O_9$ phase is easier to be dehydrated into anatase phase in the neutral solution than that in the alkaline solution under the hydrothermal conditions. The $HTMA^+$ in the interlayer space can stabilize also the layered structure.

The hydrothermally reacted products show an interesting morphology. The fibrous particles aggregated together to form cocoon-like particles with smooth surface after the hydrothermal reaction in the Ba^{2+}-free HTMA-OH solution at 150 and 200 °C (Fig. 2b and c). Cocoon-like $BaTiO_3$ particles can be obtained by the hydrothermal reaction in the $Ba(OH)_2$–(HTMA-OH) solutions at 150 and 200 °C (Fig. 2e). At 250 °C, however, no cocoon-like particle was observed in Ba^{2+}-free HTMA-OH or $Ba(OH)_2$–(HTMA-OH) solutions. At 250 °C when $H_2Ti_4O_9$ was hydrothermally reacted in Ba^{2+}-free HTMA-OH solution, the particles with similar morphology to the precursor were obtained, where without aggregation occurred (Fig. 2d). In the $Ba(OH)_2$–(HTMA-OH) solutions, the fibrous morphology of the precursor was broken down to smaller particles (Fig. 2f), due to a dissolution-deposition reaction on the surface of the particles, similar to the normal hydrothermal reaction [16]. The dissolution-deposition reaction changes the fibrous morphology of the precursor.

When $H_2Ti_4O_9$ was hydrothermally reacted in $Ba(OH)_2$–(HTMA-Br) solutions, $BaTiO_3$ phase was formed also, similar to the case of that in $Ba(OH)_2$–(HTMA-OH) solutions (Fig. 5). In the Ba^{2+}-free HTMA-Br solution, the anatase phase is formed more easily than that in the Ba^{2+}-free HTMA-OH solution. A layered titanate phase with a large basal spacing of 2.57 nm was observed (Fig. 5a), suggesting more $HTMA^+$ were intercalated into the layered titanate under the hydrothermal conditions than that at room temperature, which caused the increase of the basal spacing of the layered phase. The fibrous particles assembled together also in the $Ba(OH)_2$–(HTMA-Br) solutions, but the cocoon-like particle was not observed (Fig. 2g and h).

The above results indicate that HTMA-OH and stirring are necessary to form the cocoon-like particles. In the particle assembling process, $HTMA^+$ plays an important role in the formation of the cocoon-like particles. The surfactant ions can be adsorbed on the surface of the $H_2Ti_4O_9$ fibers, and the interaction of the hydrophobic group promotes the assembling of the fibrous particles. Under the stirring conditions, the assembled fibrous particles are shaped into the cocoon-like particles. In the $Ba(OH)_2$ solution, the layered phase of the cocoon-like particles is transformed to $BaTiO_3$ phase by the in situ topotactic reaction, but the cocoon-like particle morphology is retained after the reaction.

Conclusions

The results of this study indicate that the hydrothermal soft chemical process is useful for the preparation of $BaTiO_3$ and titanium oxide with special morphology. The cocoon-like $BaTiO_3$ and titanium oxide particles can be prepared by hydrothermally reacting fibrous $H_2Ti_4O_9$ particles in $Ba(OH)_2$–(HTMA-OH) and HTMA-OH solutions, respectively, in the temperature

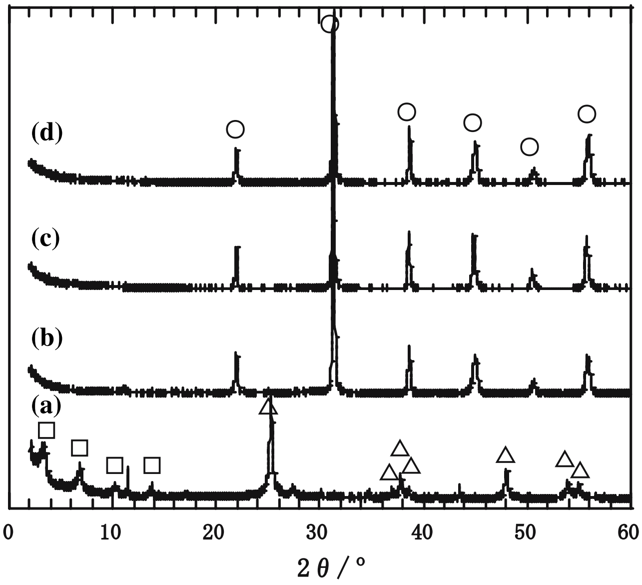

Fig. 5 X-ray diffraction patterns of products obtained by hydrothermally reacting $H_2Ti_4O_9$ in (**a**) 0, (**b**) 0.1, (**c**) 0.2, and (**d**) 0.3 M $Ba(OH)_2$–(HTMA-Br) solutions, respectively, at 150 °C for 1 day under stirring conditions. □: layered titanate phase with a basal spacing of 2.57 nm; △: anatase phase; ○: $BaTiO_3$ phase

of 150–200 °C. The cocoon-like $BaTiO_3$ and titanium oxide particles are formed by assembling fibrous $BaTiO_3$ particles and fibrous titanium oxide particles, respectively. The $HTMA^+$ in the reaction system plays an important role in the particle assembling process. The transformation reaction from the $H_2Ti_4O_9$ phase to the $BaTiO_3$ phase is topotactic structural transformation reaction.

Acknowledgement This work was supported in part by Grants-in-Aid for Scientific Research (C) (No.13650894) from Japan Society for the Promotion of Science and the Murata Science Foundation.

References

1. Phule PP, Rispud SH (1990) J Mater Sci 25:1169
2. Burfoot JC, Taylor GW (1979) Polar dielectrics and their applications. Macmillan, London
3. Kutty RN, Vivekanandan R, Murugaraj P (1998) Mater Chem Phys 19:533
4. Oledzka M, Brese NE, Riman RE (1999) Chem Mater 11:1931
5. Wu M, Long J, Wang G, Huang A, Luo Y, Feng S, Xu R (1999) J Am Ceram Soc 82:3254
6. Hernandez BA, Chang K, Fisher ER, Dorhout PK (2002) Chem Mater 14:480
7. Shimooka H, Kohiki S, Kobayashi T, Kuwabara M (2000) J Mater Chem 10:1511
8. J-F Campion, DA Payne, HK Chae And Z Xu, Ceram Trans, **22** (1191) 477 Ceramic Powder Science Iv Edited By Hirano, S, Messing, GL And Hausner, H, American Ceramic Society, Westerville OH USA
9. Sasaki T, Watanabe M, Fujiki Y, Kitami Y (1994) Chem Mater 6:1749
10. Rouxel J, Tournoux M, Brec R (1994) Soft chemical routes to new materials. Trans Tech Publications, Aedermansdorf
11. Stein A, Keller SW, Mallouk TE (1993) Science 259:1558
12. Feng Q, Kanoh H, Ooi K (1999) J Mater Chem 9:319
13. Ohara Y, Koumoto K, Yanagida H (1985) J Am Ceram Soc 68:C-108
14. Ohara Y, Koumoto K, Yanagida H (1994) J Am Ceram Soc 77:2327
15. Ohara Y, Koumoto K, Shimizu T, Yanagida H (1994) J Ceram Soc Jpn 102:88
16. Feng Q, Hirasawa M, Yanagisawa K (2001) Chem Mater 13:290
17. Feng Q, Yanagisawa K, Yamasaki N (2001) High Pressure Res 20:149