Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 4085–4092

www.elsevier.com/locate/jeurceramsoc

Synthesis of polycrystalline platelike $KNbO_3$ particles by the topochemical micro-crystal conversion method and fabrication of grain-oriented $(K_{0.5}Na_{0.5})NbO_3$ ceramics

Yasuyoshi Saito*, Hisaaki Takao

Toyota Central Research and Development Laboratories Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan

Abstract

Polycrystalline rectangular-platelike $KNbO_3$ particles with an orthorhombic perovskite structure were synthesized by the topochemical micro-crystal conversion (TMC) method from rectangular-platelike precursor particles of layer-structured $K_4Nb_6O_{17}$ at 850 °C in molten KCl-salt. TMC-synthesized $KNbO_3$ particles preserved the shape of precursor particles, and had a thickness of about 1 μm, a width of 5–10 μm and a length of 20–40 μm. However, TMC-synthesized rectangular-platelike $KNbO_3$ particles exhibited a polycrystalline morphology having preferred pseudo-cubic {0 0 1} orientation. Oriented particulate layer (OPL) X-ray diffraction analysis revealed that, in the TMC reaction, the crystallographic {0 1 0} plane of $K_4Nb_6O_{17}$, which is the largest extensive face, is converted into the {0 0 1} plane of polycrystalline $KNbO_3$ particles, which is the largest developed face, in spite of polycrystalline morphology. Using the polycrystalline rectangular-platelike $KNbO_3$ particles as template in the reactive templated grain growth method, grain-oriented $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO ceramics having a pseudo-cubic {0 0 1} orientation degree (Logering's factor) of 39.7% could be fabricated. The result indicates that not only single crystalline particles, which were generally used, but also the polycrystalline particles can be act as template in the templated grain growth process. The availability of polycrystalline particles will give a new synthesis design of templates for texturing of various kinds of ceramics.

Keyword: Platelike $KNbO_3$ particle; Niobates; Perovskites; Piezoelectric properties

1. Introduction

The synthesis of platelike particles is of great attraction due to their usage as template particles in the texturing of grain-oriented ceramics for improving the electrical properties (piezoelectricity, dielectricity, etc.) of various materials, such as the perovskite structured materials having a pseudo-cubic crystal structure. However, regular-perovskite structured materials typically grow as equiaxed particles,[1] and it is difficult to synthesized platelike particles using conventional methods such as flux method, hydrothermal method and so on. Potassium niobate, $KNbO_3$ (KN), is a perovskite-structured ferroelectrics with an orthorhombic crystal phase at room temperature, and has a high Curie temperature (>400 °C). Hence, it is used as a end member of perovskite structured (K, Na)NbO_3 lead-free piezoelectric family materials.[2–18]

One of exiting applications of anisotropically shaped particles, such as platelike particles, is as templates in templated grain growth (TGG)[19,20] and reactive templated grain growth (RTGG)[21–25] of textured polycrystalline ceramics and as templates in seeded polycrystal conversion (SPC)[26,27] of single-crystals. In the TGG and RTGG method, the initial degree of orientation of the template particles in the matrix powder is very important to increase degree of orientation in textured ceramics. Initial template orientation is achieved by the shear stress comes from the anisotropical shape during tape casting, which results in oriented grain growth. Thus, it is crucial synthesizing an anisotropically shaped template in the grain growth method for fabricating textured ceramics.

Regarding the synthesis of platelike $NaNbO_3$ particles, recently we proposed a new technique for the synthesis of platelike $NaNbO_3$ particles using our developed topochemical micro-crystal conversion (TMC) method.[3,6] This technique preserves and/or inherits the particle shape from an anisotropi-

---

* Corresponding author at: Inorganic Laboratory, Materials Department, Toyota Central Research and Development Laboratories Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan. Tel.: +81 561 63 4821;
fax: +81 561 63 5743.

E-mail address: ysaito@mosk.tytlabs.co.jp (Y. Saito).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.02.099

cally shaped precursor (platelike $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ particles) to the objective compound particle (platelike $NaNbO_3$) through a topochemical, topotactic and/or pseudomorphic reaction while the chemical composition of the particle is varied. About non-anisotoropically shaped $KNbO_3$ particles, many preparation methods were reported, such as hydrothermal,[28–31] sol–gel,[32,33] glycothermal[34] and polymerized complex method.[35] With regard to the synthesis of platelike $KNbO_3$ particles, nanoneedles and nanoplatelets of pseudo-cubic $KNbO_3$ was reported by the polymerized complex method from $K_4Nb_6O_{17}$ precursor.[36] However, there is no report of synthesizing the micro-meter-sized platelike $KNbO_3$ particles having the orthorhombic perovskite crystal structure, which is the suitable size to use as templates in fabricating textured ceramics. To fabricate micro-meter-sized platelike $KNbO_3$ particles, we selected layer-structured $K_4Nb_6O_{17}$ as precursor particles in the TMC method, because this material was reported as layer structured material and was widely studied as host materials of ion intercalation, nanosheets formation by exfoliation and photo-catalyst applications.[37–40]

In this paper, we first report the results of conversion from $K_4Nb_6O_{17}$ to $KNbO_3$ particles by the TMC method from the viewpoint of particle shape inheritance. Then, we describe the fabrication of grain-oriented $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO ceramics using TMC-synthesized platelike $KNbO_3$ particles as a template in the RTGG method. Finally, we discuss the conversion mechanism from $K_4Nb_6O_{17}$ to $KNbO_3$ particles in the TMC reaction.

2. Experimental procedure

2.1. Synthesis of platelike $KNbO_3$ particles

We design a new synthesis route from $K_4Nb_6O_{17}$ to $KNbO_3$ particles by the TMC method. First, platelike $K_4Nb_6O_{17}$ (K4N6) precursor particles were prepared by molten salt synthesis at 1050 °C for 2 h according to the following equation:

$$2K_2CO_3 + 3Nb_2O_5 \rightarrow K_4Nb_6O_{17} + CO_2.$$

In this synthesis reaction, K_2CO_3 (Aldrich, Milwaukee, WI, USA, 99.99%) and Nb_2O_5 (Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan, 99.99%) were used as raw materials and KCl (Wako Pure Chemical Industries Ltd., Osaka, Japan, 99.5%) salt was used as a flux. A mixture of 1:1 (w/w) of objective oxide powder of final product to salt was used in the molten salt synthesis. Repeated hot-water washing and decantation was employed to remove the KCl flux during filtration. Next, using platelike $K_4Nb_6O_{17}$ precursor particles, the topochemical micro-crystal conversion from $K_4Nb_6O_{17}$ to $KNbO_3$ was carried out according to the following reaction scheme at 850 °C for 8 h in a molten KCl flux:

$$K_4Nb_6O_{17} + (1+x)K_2CO_3 \rightarrow 6KNbO_3 + xK_2CO_3 + 2CO_2,$$

where x was selected as 1.0, 1.2, 1.5 in order to determine the full conversion condition from precursor $K_4Nb_6O_{17}$ to $KNbO_3$. To remove both the KCl flux and the excess amount of K_2CO_3, repeated hot-water washing and decantation on the filter was performed. Finally, successive filtration applied to isolate synthesized $KNbO_3$ particles. To compare the present TMC method and the conventional method with respect to particle shape, we synthesized $KNbO_3$ particles by the conventional flux method at 950 °C for 2 h in a molten KCl flux according to the following equation:

$$K_2CO_3 + Nb_2O_5 \rightarrow 2KNbO_3 + CO_2.$$

The shape and atomic composition of synthesized particles were observed by scanning electron microscopy (SEM; S-3600N, Hitachi, Japan) equipped with energy-dispersive X-ray spectrometer (EDX). The crystalline phases were determined by X-ray diffraction analysis (XRD; Rint-TTR, Rigaku, Japan) using Cu Kα radiation. The largest extensive planes of the particles were determined by XRD of an oriented particulate layer (OPL) cast on a glass plate with gelatin (OPL-XRD).[41]

2.2. Fabrication of textured $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO ceramics

Textured $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO ceramics (hereafter described as KNN–1% CuO), where CuO is a sintering aid, were fabricated by the reactive templated grain growth method with the use of TMC-synthesized polycrystalline platelike $KNbO_3$ particles as a template. The fraction of the $KNbO_3$ template was selected as 10 at.% for the B-site element of Nb according to the following equation:

$$\begin{aligned}&0.5\{0.9KNbO_3(\text{matrix}) + 0.1KNbO_3(\text{template})\}\\&\quad + 0.5NaNbO_3(\text{matrix}) + 0.01CuO\\&\quad \rightarrow (K_{0.5}Na_{0.5})NbO_3\text{–}0.01CuO(\text{ceramics})\end{aligned}$$

The complementary matrix powder, i.e., equiaxed $KNbO_3$ and $NaNbO_3$ particles having an average grain size of 0.5 μm, were prepared from raw powders of K_2CO_3 (Aldrich, 99.99%), Na_2CO_3 (Rare Metallic, Tokyo, Japan, 99.99%) and Nb_2O_5 (Kojundo Chemical Laboratory Co. Ltd., 99.99%) by ball-mill crushing for 24 h in an acetone solution with zirconia balls of 3 mm diameter, which was followed by ball-mill mixing for 24 h in an acetone solution with zirconium oxide balls of 10 mm diameter, filtering, drying in oven at 90 °C for 1 day and heated at 750 °C for 5 h in air. CuO (Kojundo Chemical Laboratory Co. Ltd., 99.99%) powder was used as the sintering aid.

The template particles and matrix powders were mixed in a solvent (45 vol% ethanol and 55 vol% toluene), binder (polyvinyl butyral, Sekisui Chemical, Japan, BH-3) and plasticizer (di-butyl phthalate, Wako Pure Chemical Industries Ltd.) to form a slurry. The slurry was tape-cast by a doctor blade apparatus (DP-150, Tsugawa Seiki, Tokyo, Japan). After drying, a single-layer sheet with a thickness of about 80 μm was cut, laminated and hot-pressed at a temperature of 80 °C and a pressure of 9.8 MPa for 10 min to form a 2 mm thick green compact. The compacts were further cut into small samples of about 5 mm width and 15 mm length. The compacts were heated at 600 °C for 1 h to remove organic substances prior to sintering, and then were soaked at various temperatures between 1000 and 1175 °C for 1 h in O_2 atmosphere, brought to temperature at a heating rate of 200 °C/h.

Apparent densities of the samples were measured by the Archimedean method. The measured XRD density of non-textured KNN–1% CuO ceramics (4.506 g/cm^3)[5] was used to calculate the relative density. The crystalline phases and the degree of texture development were determined by XRD analysis using Cu Kα radiation. The degree of pseudo-cubic $\{0\,0\,1\}$ orientation of the textured KNN–1% CuO ceramics, F, was evaluated by Lotgering's equation,[42]

$$F = \frac{P - P_0}{1 - P_0}$$

where P is the sum $I(0\,0\,h)$/sum $I(h\,k\,l)$, P_0 the sum $I_0(0\,0\,h)$/sum $I_0(h\,k\,l)$ and sum I is the summation of the peak intensities of the XRD pattern on the grinded surface of the sintered specimen. Sum I_0 is the summation of the XRD peak intensities of the equiaxed reference powder. Diffraction peaks between $2\theta = 5°$ and $70°$ were used for the calculations. The microstructure of a side-surface perpendicular to the tape-casting plane was observed using scanning electron microscopy (SEM).

Rectangular-shaped specimens with a thickness of 0.6 mm, a width of 3 mm and a length of 12 mm were fabricated from the sintered specimens. The upper and lower surfaces of rectangular-shaped specimen were parallel to tape-casting plane and coated with Au electrode by sputtering for electrical property measurements. Resistivities were measured by the two-probe method at 5 V/mm using an ultra-high resistance meter (R8340A, Advantest) before poling treatment. The specimens were poled at 100 °C by immersion in silicon oil under a dc electric field of 3 kV/mm for 10 min. The dielectric constant and dielectric loss were determined using an impedance analyzer (HP4194A, Agilent). The piezoelectric constant d_{33} was measured at room temperature by the direct piezoelectric method using a piezo-d_{33} meter (ZJ-4B, Academia Sinca). All properties were measured using 1-day-aged samples. For a comparison, non-textured $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO ceramics was fabricated by the conventional ceramics process sintered at 1050 °C for 1 h in O_2 atmosphere. A disk-shaped specimens with a thickness of 0.5 mm and diameter of 11 mm were fabricated from the sintered specimens, and coated with Au electrodes on both upper and bottom surface. The same characterizations were performed, and the measured data were compared with those of the textured ceramics.

3. Results and discussion

3.1. Synthesis of platelike $KNbO_3$ particles

Fig. 1a shows an SEM image of $KNbO_3$ particles synthesized by the conventional flux method at 950 °C. This method only gives equiaxed and cube-shaped $KNbO_3$ particles; it is

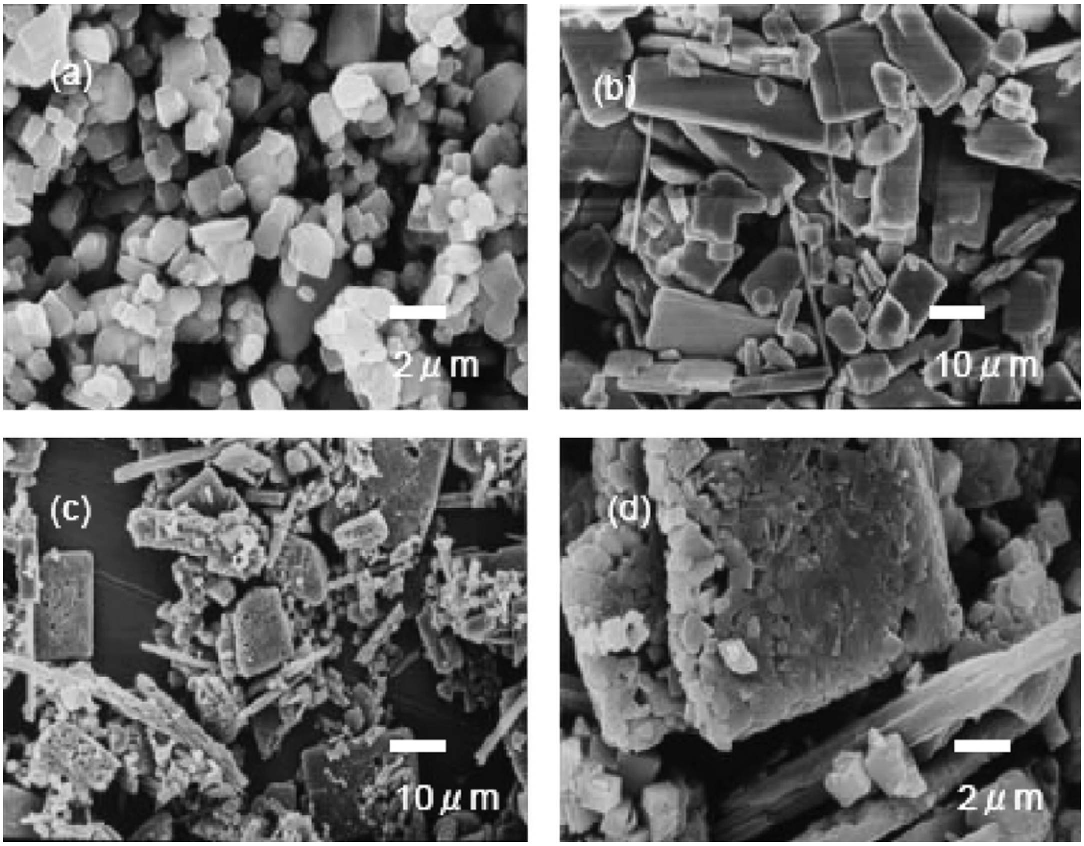

Fig. 1. SEM images. (a) $KNbO_3$ particles synthesized by the conventional flux method at 950 °C for 2 h. (b) $K_4Nb_6O_{17}$ precursor particles prepared by molten salt synthesis at 1050 °C for 2 h. (c and d) Platelike $KNbO_3$ particles synthesized by the topochemical micro-crystal conversion method from $K_4Nb_6O_{17}$ precursor particles at 850 °C for 8 h.

not able to synthesize platelike particles. The crystalline phase of these particles is an orthorhombic perovskite $KNbO_3$ structure, as determined by the XRD pattern shown in Fig. 2a. Fig. 1b shows an SEM image of $K_4Nb_6O_{17}$ particles prepared by the flux method at 1050 °C. $K_4Nb_6O_{17}$ can be fabricated as rectangular-platelike particles with a width of 5–10 μm, a length of 20–40 μm and a thickness of 0.5–1 μm. The particles have a layer $K_4Nb_6O_{17}$ structure assigned by the XRD pattern shown in Fig. 2b, which is identified by JCPDS powder diffraction file card No. 76-0977. Fig. 1c shows a SEM image of TMC-synthesized $KNbO_3$ particles at the reaction condition of $x = 1.2$. The particles exhibit a platelike shape with a width of 5–10 μm, a length of 20–40 μm and a thickness of 0.5–1 μm. However, the particles have a polycrystalline structure which are built up by many grains having an averaged grain size of about 0.5 μm, and inherited the $K_4Nb_6O_{17}$ precursor's shape without breaking into individual smaller particles.

The crystalline phase of the particles is an orthorhombic perovskite structured $KNbO_3$, as determined by the XRD pattern shown in Fig. 2e and d, which is identified by JCPDS powder diffraction file card No. 32-0832. However, full conversion from $K_4Nb_6O_{17}$ to $KNbO_3$ were obtained at reaction conditions of $x = 1.2$ and 1.5 shown in Fig. 2d and e. At $x = 1.0$, the unconverted $K_4Nb_6O_{17}$ remains in synthesized particles shown in Fig. 2c. These data mean that polycrystalline platelike $KNbO_3$ particles having single perovskite crystal phase can be synthesized through the TMC reaction under the reaction condition of x above $x = 1.2$, in which $KNbO_3$ formed by K ion diffusing into $K_4Nb_6O_{17}$ crystal with preserved particle outer-shape and a developed plane. To identify the largest developed planes of $K_4Nb_6O_{17}$ and TMC-synthesized $KNbO_3$ particles, we measured XRD patterns of particles that were cast on glass substrates, which is called oriented particulate layer X-ray diffraction measurement technique.[42] In this casting method (OPL-XRD method), the largest developed plane of the particles is easily aligned with the glass plane. Fig. 3 shows the XRD patterns of cast $K_4Nb_6O_{17}$ and $KNbO_3$ particles, in comparison with JCPDS patterns of $K_4Nb_6O_{17}$ (#76-0977) and $KNbO_3$ (#32-0832), respectively. These patterns indicate that the developed plane of $K_4Nb_6O_{17}$ is the {0 1 0} plane

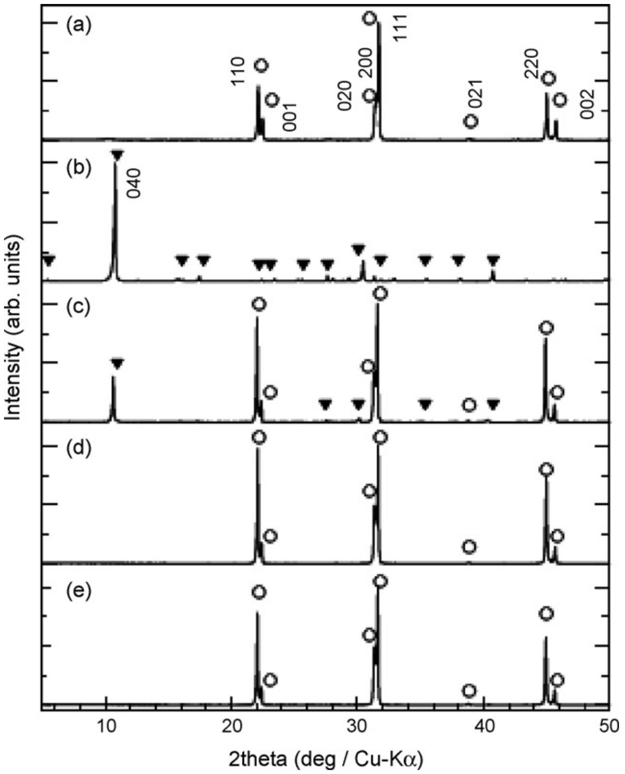

Fig. 2. X-ray diffraction patterns. (a) $KNbO_3$ particles synthesized by the conventional flux method at 950 °C for 2 h. (b) $K_4Nb_6O_{17}$ precursor particles prepared by molten salt synthesis at 1050 °C for 2 h. (c) Platelike $KNbO_3$ particles synthesized by the topochemical micro-crystal conversion method from $K_4Nb_6O_{17}$ precursor particles at 850 °C for 8 h; $x = 1.0$, (d) $x = 1.2$, (e) $x = 1.5$, (○) $KNbO_3$, (▼) $K_4Nb_6O_{17}$.

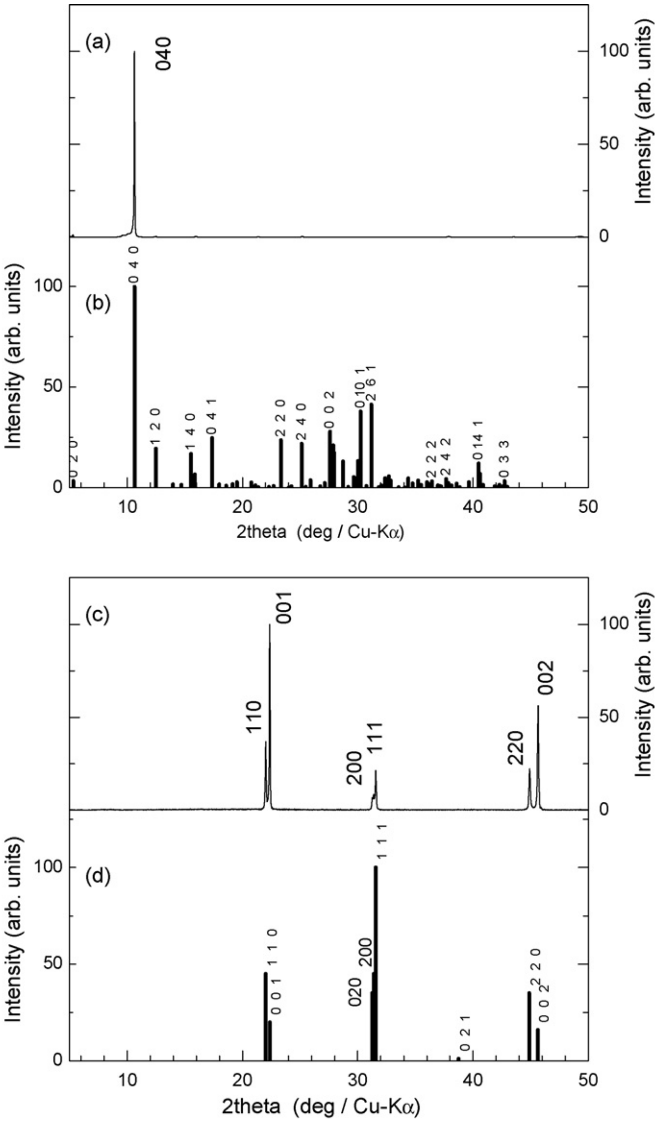

Fig. 3. X-ray diffraction patterns. (a) $K_4Nb_6O_{17}$ precursor particles cast on a glass substrate. (b) $K_4Nb_6O_{17}$ pattern of JCPDS powder diffraction file #76-0977. Major Miller indices are shown. (c) Platelike $KNbO_3$ particles synthesized by the topochemical micro-crystal conversion method from $K_4Nb_6O_{17}$ precursor particles cast on a glass substrate. (d) $KNbO_3$ pattern of JCPDS powder diffraction file #32-0832.

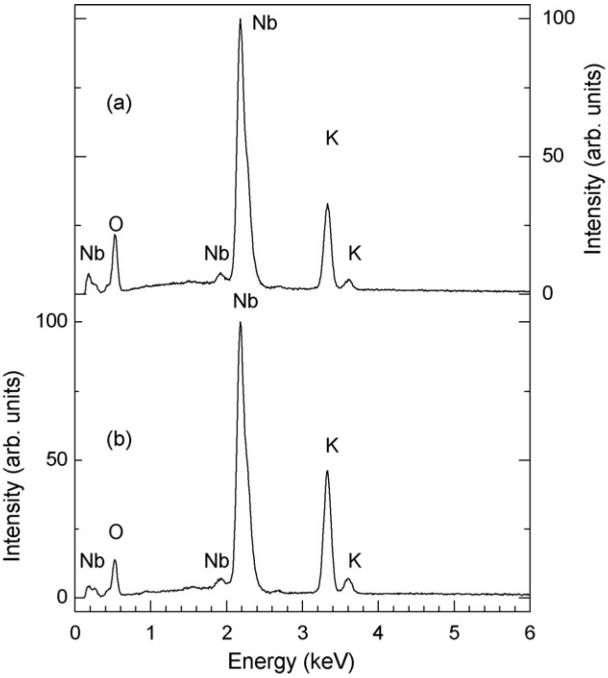

Fig. 4. . Energy-dispersive X-ray spectroscopy (EDX) profiles. (a) $K_4Nb_6O_{17}$ precursor particles prepared by molten salt synthesis at 1050 °C for 2 h. (b) Platelike $KNbO_3$ particles synthesized by the topochemical micro-crystal conversion method from $K_4Nb_6O_{17}$ precursor particles at 850 °C for 8 h.

because of observation of larger (0 4 0) peaks in cast particles than that of JCPDS pattern. And the major developed plane of TMC-synthesized $KNbO_3$ with polycrystalline morphology is the {0 0 1} plane. This means that the grains in polycrystalline particle statistically preferably aligned or oriented along ⟨0 0 1⟩ axis in a pseudo-cubic notation in each particle. This suggests that, during the TMC reaction, the {0 1 0} plane of single crystalline $K_4Nb_6O_{17}$ is converted into the preferred pseudo-cubic {0 0 1} plane of polycrystalline $KNbO_3$ particles.

Table 1
Atomic compositions of $K_4Nb_6O_{17}$ precursor particles and platelike $KNbO_3$ particles synthesized by the topochemical micro-crystal conversion method from the precursor particles, as measured by energy-dispersive X-ray spectroscopy (EDX)

Sample	Atom				
	K (at.%)		Nb (at.%)		K:Nb ratio
	Average	Deviation	Average	Deviation	
$K_4Nb_6O_{17}$	40.6	0.1	59.4	0.1	4.11:6
$KNbO_3$	49.0	0.9	51.0	0.9	0.96:1

To evaluate the change of atomic ratio of K:Nb during the TMC reaction in the particles, we measured the EDX profiles of both $K_4Nb_6O_{17}$ and TMC-synthesized $KNbO_3$ particles. Fig. 4 shows EDX measurement profiles. K, Nb and O peaks were observed in the EDX profiles. K atom's peak of $K_4Nb_6O_{17}$ is larger than that of TMC-synthesized polycrystalline $KNbO_3$. Table 1 shows the calculated averaged results of K and Nb atomic composition with use of five measurement data. It shows that the K:Nb ratio in $K_4Nb_6O_{17}$ and TMC-synthesized $KNbO_3$ particles are 4.11:6 and 0.96:1, respectively. These values are in good accordance with designed composition of $K_4Nb_6O_{17}$ and $KNbO_3$ as taking account of measurement error level.

The reason of formation of polycrystalline $KNbO_3$ particles having preferred {0 0 1} orientation during TMC reaction from $K_4Nb_6O_{17}$ to $KNbO_3$ can be explained using the crystal structures shown in Fig. 5. In the TMC reaction, plane of {0 1 0} $K_4Nb_6O_{17}$ converts to preferred oriented plane of {0 0 1} $KNbO_3$. The structure of $K_4Nb_6O_{17}$ could be characterized as a stacking of $–Nb_6O_{17}–$ sheets consisted of corner-sharing and edge-sharing NbO_6 octahedra, and K atoms are located between the $–Nb_6O_{17}–$ sheets. In each sheet, NbO_6 octahedron units connect with alternately sharing corners and edges along the [0 0 1] direction, and connect with sharing corners (and shearing corners) along the [1 0 0] direction. In the perovskite $KNbO_3$ crystal, NbO_6 octahedron units connect with sharing corners

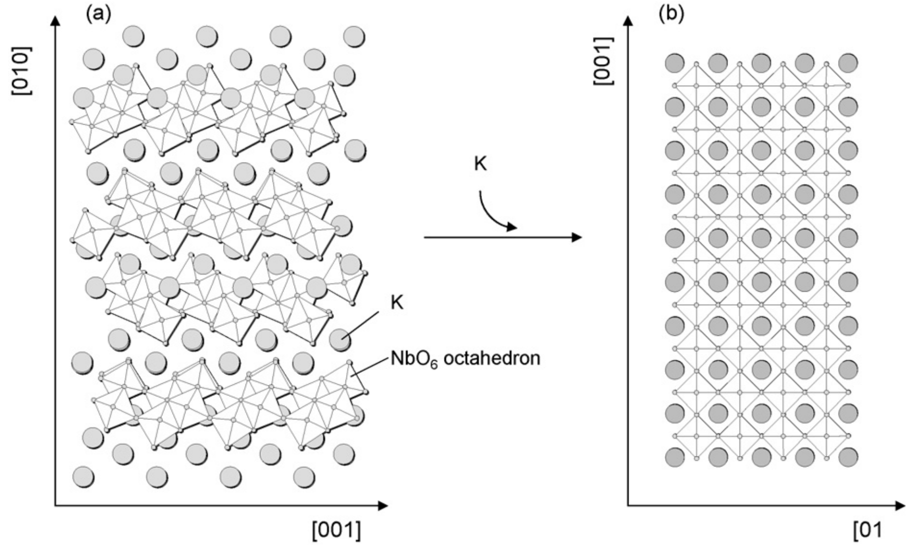

Fig. 5. Schematic crystal structure and reaction scheme. (a) Layer-structured $K_4Nb_6O_{17}$ along the [1 0 0] direction and (b) perovskite-structured $KNbO_3$.

along the [0 0 1], [0 1 0] and [0 0 1] directions. When TMC reaction occurs in $K_4Nb_6O_{17}$ crystal, K atoms must need to diffuse inside the $K_4Nb_6O_{17}$ crystal probably through along the plane of sheet direction, because $K_4Nb_6O_{17}$ has a K atom composition deficient compared to the $KNbO_3$. During conversion, the bonds of edge-sharing NbO_6 octahedra inside $–Nb_6O_{17}–$ sheets along the [0 0 1] direction must be separated, and NbO_6 octahedra would rotate, and then the bonds of corner-sharing NbO_6 octahedra inside $–Nb_6O_{17}–$ sheet re-connected. And the new-bonds of corner-sharing NbO_6 octahedra between $–Nb_6O_{17}–$ sheets must newly generated accompanying with the diffusion of K atoms inside $–Nb_6O_{17}–$ sheets. These bond-breaking of edge-sharing bond, re-bonding of corner-sharing bond inside the sheets associated with rotation of NbO_6 octahedron units along the [0 0 1] direction, new-generation of corner-sharing bonds of NbO_6 octahedron units between the sheets, and K atoms diffusion are very complicated to be perfectly understood. At least, it is assumed that the three-dimensional volume of same rotation direction (or same tilting direction) of NbO_6 octahedron units along the [0 0 1] direction is limited. As a result, it could give the polycrystalline structure and determined the grain size of about 0.5 μm during conversion reaction from layer structured $K_4Nb_6O_{17}$ to perovskite structured $KNbO_3$. However, more future experiments are needed to explain full atomic movements during the conversion reaction.

As TMC-synthesized $KNbO_3$ particles have polycrystalline morphology, however, it has preferred $\{0\,0\,1\}$ oriented plane in each particle. Therefore, the TMC-synthesized particles have a possibility to act as template in templated grain growth process. Next section, I will report the result of fabrication of textured ceramics using the TMC-synthesized particles.

3.2. *Fabrication of textured $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO ceramics*

Fig. 6a and b shows the XRD patterns of the surfaces of non-textured and textured $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO ceramics sintered at 1050 and 1175 °C for 1 h in O_2, respectively. The fraction of $KNbO_3$ template in the RTGG method is 10%. Larger peaks of (1 1 0), (0 0 1), (2 2 0) and (0 0 2), which are re-indexed as $\{0\,0\,1\}$ plane in pseudo-cubic perovskite notation, are observed in textured ceramics than those peaks in non-textured ceramics. The calculated Lotgering's factor of the $\{0\,0\,1\}$ orientation in pseudo-cubic notatin is 39.7%.

Fig. 7 shows a comparison of SEM images between non-textured and textured ceramics. The shape of grains in two samples can be seen to be similar rectangular shape. However, grains in non-textured ceramics exhibit non-uniform grain growth, whereas the grains in textured ceramics display a uniform growth pattern. The averaged grain size of about 20 μm in textured ceramics are nearly two times larger than that of the maximum grain size of 10 μm in non-textured ceramics. The reason of the larger grain size in textured ceramics comes from higher sintering temperature. The more uniformed grain growth in textured ceramics could be attributed to a uniform distribution of the template particles in the green ceramic body, which was followed by the uniform nucleation of grain growth

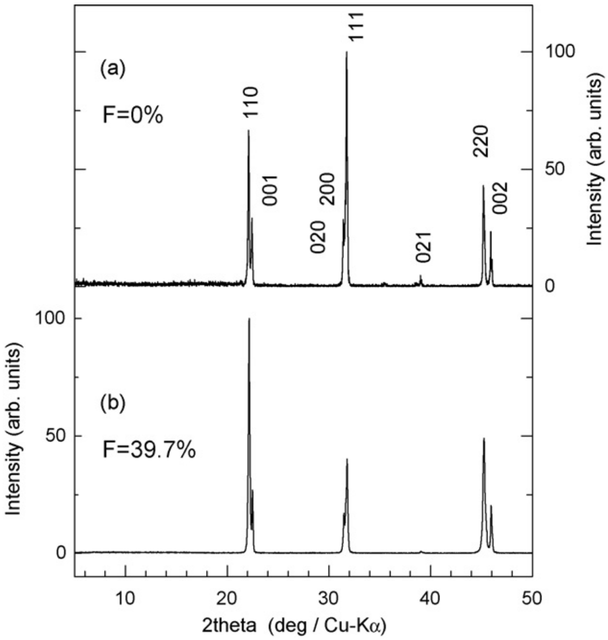

Fig. 6. XRD profiles of surfaces of $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO ceramics. (a) Non-textured ceramic sintered at 1050 °C for 1 h. (b) Textured ceramics sintered at 1175 °C for 1 h. The XRD profiles are assigned using orthorhombic Miller indices. F is the degree of pseudo-cubic $\{0\,0\,1\}$ orientation.

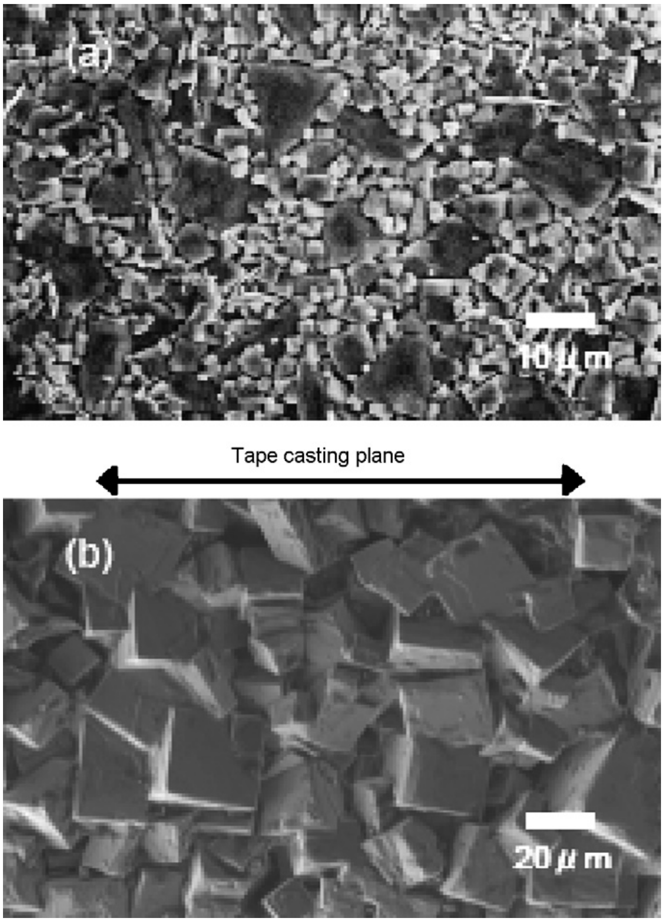

Fig. 7. SEM images of $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO ceramics. (a) SEM image of sintered surface of non-textured ceramic sintered at 1050 °C for 1 h. (b) SEM image of side-surface of textured ceramics sintered at 1175 °C for 1 h.

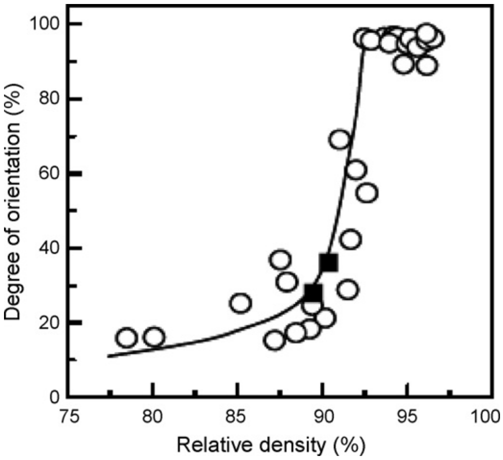

Fig. 8. Degree of pseudo-cubic {0 0 1} orientation of textured $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO ceramics sintered at 1000–1175 °C in O_2 atmosphere as a function of relative density. (○) Previously reported our data,[6] (■) this work.

at each grain. However, relative density of textured ceramics had fall short of full density, which is 90.5 % of relative density. Fig. 8 shows relation between degree of orientation and relative density for textured ceramics in $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO composition along with our previously reported data in $(K_{0.5}Na_{0.5})NbO_3$ and $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO composition that were taken from the samples fabricated by RTGG method using $NaNbO_3$ template.[6]

As shown in Fig. 8, we reported in a previous paper that (open circles are our previously reported data), in the region below around a relative density of 90%, the orientation degree increases gradually up to around 30% with a small raising rate, but it increases abruptly to beyond 92% at higher relative density region along with the solid-line curve. The samples fabricated in this paper were plotted as a closed square, and it is clear that the data are in good agreement with the solid curve. This means that one of the reason of not so large {0 0 1} orientation degree of 39.7% is its low relative density of 90.5% due to inhibition of densification during sintering by the large TMC-synthesized $KNbO_3$ templates.

The dielectric, piezoelectric and insulation properties of non-textured and textured KNN–1% CuO specimens are listed in Table 2. It can be seen that the piezoelectric properties of the textured specimen – d_{33} and g_{33} – are not enhanced by a texturing, because of its low relative density of 90.5%. However, the resistivity is a large value of 1.75×10^{13} Ω cm, and this enabled to pole the sample at 3 kV/mm in 100 °C oil without an electrically breakdown. In the future experiment, we will try to increase relative density by means of a hot-press sintering method or hot-isostatically press sintering method, and to clear the limit of orientation degree in the case of using the TMC-synthesized polycrystalline platelike $KNbO_3$ template particles.

Table 2
Dielectric, insulation and piezoelectric properties of textured and non-textured $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO ceramics

Material property	Textured	Non-textured
{1 0 0} Orientation factor (%)	39.7	0
Relative density (%)	90.5	99.2
Dielectric constant	306	231
Dielectric loss (%)	0.94	0.32
Piezoelectric d_{33} constant (pC/N)	68	86
Piezoelectric g_{33} constant (10^{-3} V m/M)	25.1	42.1
Resistivity (Ω cm)	1.75E + 13	1.30E + 13

4. Conclusions

We designed a new synthesis route for fabricating platelike $KNbO_3$ particles with an orthorhombic perovskite structure by the topochemical micro-crystal conversion (TMC) method from platelike precursor particles of layer-structured $K_4Nb_6O_{17}$. The TMC method yields polycrystalline rectangular-platelike $KNbO_3$ particles whose outer-shape preserved the shape of the precursor particles and had a thickness of about 0.5–1 μm, a width of 5–10 μm and a length of 20–40 μm. Oriented particulate layer X-ray diffraction analysis revealed that in the TMC reaction, the crystallographic {0 1 0} plane of $K_4Nb_6O_{17}$ is converted into the most of {0 0 1} plane of polycrystalline $KNbO_3$ particles in spite of polycrystalline morphology. Using the polycrystalline platelike $KNbO_3$ particles as a template in the reactive templated grain growth method, {0 0 1} grain-oriented $(K_{0.5}Na_{0.5})NbO_3$–1 mol% CuO ceramics having a pseudo-cubic {0 0 1} orientation degree (Logering's factor) of 39.7% could be fabricated. This indicates that the polycrystalline particles can be act as template in the templated grain growth process. In other word, we can fabricate the textured ceramics by using the polycrystalline template particles. The result that the polycrystalline particles are available in the templated grain growth method will open new designs of preparation of template particles for texturing of various ceramic materials.

References

1. Bishop, C., *An Outline of Crystal Morphology*. Hutchinson Scienctific and Techinical, London, United Kingdom, 1967.
2. Hellwege, K. H., Hellwege, A. M., Mitsui, T. and Nomura, S., ed., *Numerical Data and Functional Relationships in Science and Technology New Series, Group 3: Crystal and Solid State Physics, Vol. 16, Ferroelectrics and Related Substances, Vol. a, Oxides*. Springer, Berlin, 1981.
3. Saito, Y., Takao, H., Tani, T., Nonoyama, T., Takatori, K., Homma, H. *et al.*, Lead-free piezoceramics. *Nature*, 2004, **432**(4), 84–87.
4. Saito, Y., *Piezoelectric material composition of alkali metal-containing niobium oxide*, Japan Patent Application, 2000-313664, 2000 [in Japanese]; Saito, Y., *Alkali metal-containing niobate-based piezoelectric material composition and a method for producing the same*, United States Patent, 6-387-295, 2002.
5. Saito, Y. and Takao, H., Nb-perovskite structured piezoelectric ceramics for sensor and actuator. In *The 12th US–Japan Seminar on Dialectric and Piezoelectric Ceramics Program Summary and Extended Abstracts*, 2005, pp. 103–107.
6. Takao, H. and Saito, Y., Microstructural evolution of crystalline-oriented $(K_{0.5}Na_{0.5})NbO_3$ piezoelectric ceramics with sintering aid of CuO. *J. Am. Ceram. Soc.*, 2006, **89**(6), 1951–1956.
7. Egerton, L. and Dillon, D. M., *J. Am. Ceram. Soc.*, 1959, **42**, 438–442.
8. Jaeger, R. E. and Egerton, L., *J. Am. Ceram. Soc.*, 1962, **45**(5), 209–213.
9. Dungan, R. H. and Golding, R. D., *J. Am. Ceram. Soc.*, 1965, **48**(11), 601.
10. Haertling, G. H., *J. Am. Ceram. Soc.*, 1967, **50**(6), 329–330.
11. Egerton, L. and Bieling, C. A., *Ceram. Bull.*, 1968, **47**(12), 1151–1156.

12. Tashiro, S., Nagamatsu, H. and Nagata, K., *Jpn. J. Appl. Phys.*, 2002, **41**(11B), 7113–7118 (Part 1).
13. Guo, Y., Kakimoto, K. and Ohsato, H., *Appl. Phys. Lett.*, 2004, **85**, 4121–4123.
14. Guo, Y., Kakimoto, K. and Ohsato, H., *Jpn. J. Appl. Phys.*, 2004, **43**(9B), 6662–6666.
15. Guo, Y., Kakimoto, K. and Ohsato, H., *Solid State Commun.*, 2004, **129**, 279.
16. Matsubara, M., Yamaguchi, T., Kikuta, K. and Hirano, S., *Jpn. J. Appl. Phys.*, 2004, **43**, 7159.
17. Matsubara, M., Yamaguchi, T., Kikuta, K. and Hirano, S., *Jpn. J. Appl. Phys.*, 2005, **44**, 258.
18. Matsubara, M., Yamaguchi, T., Kikuta, K. and Hirano, S., *Jpn. J. Appl. Phys.*, 2005, **44**, 6136.
19. Brahmaroutu, B., Messing, G. L., Trolier-Mckinstry, S. and Selvaraj, U., In *Proceedings of the 10th IEEE International Symposium on Applications of Ferroelectrics, Vol. 2*, ed. B. Kulwicki, A. Amin and A. Safari. Institute of Electrical and Electronic Engineers (IEEE), Piscataway, NJ, 1996, pp. 883–886.
20. Horn, J. A., Zhang, S. C., Selvaraj, U., Messing, G. L. and Trolier-McKinstry, S., *J. Am. Ceram. Soc.*, 1999, **82**, 921.
21. Kimura, T., Yoshimoto, T., Iida, N., Fujita, Y. and Yamaguchi, T., *J. Am. Ceram. Soc.*, 1989, **72**, 85.
22. Watanabe, H., Kimura, T. and Yamaguchi, T., *J. Am. Ceram. Soc.*, 1991, **74**, 139.
23. Tani, T., *J. Korean Phys. Soc.*, 1998, **32**(Suppl.), S1217–S1220.
24. Takeuchi, T., Tani, T. and Saito, Y., *Jpn. J. Appl. Phys.*, 1999, **38**, 5553.
25. Sugawara, T., Shimizu, M., Kimura, T., Takatori, K. and Tani, T., *Ceram. Trans.*, 2003, **136**, 389.
26. Li, T., Scotch, A. M., Harmer, M. P., Chan, H. M., Park, S., Shrout, T. R. *et al.*, *J. Am. Ceram. Soc.*, 1998, **81**(1), 244.
27. Li, T., Wu, S., Khan, A., Scotch, A. M., Chan, H. M. and Harmer, M. P., *J. Mater. Res.*, 1999, **14**(8), 3189.
28. Kormarneri, S., Roy, R. and Li, Q. H., *Mater. Res. Bull.*, 1992, **27**, 1393.
29. Lu, C. H., Lo, S. Y. and Lin, H. C., *Mater. Lett.*, 1998, **34**, 172.
30. Goh, G. K. L. and Langne, F. F. J., *J. Mater. Res.*, 2003, **18**, 338.
31. Uchida, S., Inoue, Y., Fujisiro, Y. and Saito, T., *J. Mater. Sci.*, 1998, **33**, 5125.
32. Nazcri-Eshghi, A., Kuang, A. X. and Mackenzic, J. D., *J. Mater. Sci.*, 1990, **25**, 3333.
33. Amini, M. M. and Sacks, M. D., *J. Am. Ceram. Soc.*, 1991, **74**, 53.
34. Lu, C. H., Lo, S. Y. and Wang, Y. L., *Mater. Lett.*, 2002, **55**, 121.
35. Simoes, A. Z., Ries, A., Riccardi, C. S., Gonzalez, A. H., Zaghete, M. A., Stojanovic, B. D. *et al.*, *Mater. Lett.*, 2004, **58**, 2537.
36. Privosic, I., Makovec, D. and Drofenik, M., Formation of nanoneedles and nanoplatelets of $KNbO_3$ perovskite during templated crystallization of the precursor gel. *Chem. Mater.*, 2005, **17**, 2953–2958.
37. Kato, R., Kuroda, K. and Ogawa, M., Unidirectional orientation of Methylene Blue intercalated in $K_4Nb_6O_{17}$ single crystal. *J. Phys. Chem. B*, 2003, **107**, 4043–4047.
38. Miyamoto, N., Yamamoto, H., Kato, R. and Kuroda, K., Formation of extraordinarily large nanosheets from $K_4Nb_6O_{17}$ crystals. *Chem. Commun.*, 2002, **20**, 2378–2379.
39. Domen, K., Kudo, A., Shinozaki, A., Tanaka, A., Maruya, K. and Onishi, T., *J. Chem. Soc. Chem. Commun.*, 1986, 356.
40. Saupe, G. B., Waraksa, C. C., Kim, H. N., Han, Y. J., Kaschak, D. M., Skinner, D. M. *et al.*, *Chem. Mater.*, 2000, **12**, 1556.
41. Sugimoto, T., Muramatsu, A., Sakata, K. and Shindo, D., Characterization of hematite particles of different shapes. *J. Colloid Interface Sci.*, 1993, **158**, 420–428.
42. Lotgering, F. K., *J. Inorg. Nucl. Chem.*, 1959, **9**(2), 113.