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Synthesis of platelike $CaTiO_3$ particles by a topochemical microcrystal conversion method and fabrication of textured microwave dielectric ceramics

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Abstract

Platelike $CaTiO_3$ particles with an orthorhombic perovskite structure have been synthesized by topochemical microcrystal conversion (TMC) from platelike precursor particles of the layer-structured $CaBi_4Ti_4O_{15}$ at 950 °C. The $CaTiO_3$ particles inherited and retained the shape of the precursor particles with a thickness of approximately 0.3 μm, and a width of 2–6 μm. XRD analysis showed that in the TMC reaction, the crystallographic {0 0 1} plane of $CaBi_4Ti_4O_{15}$ is converted into the {1 0 0} plane of $CaTiO_3$. Using the platelike $CaTiO_3$ particles as templates in the templated grain growth method, dense {1 0 0} grain-oriented $CaTiO_3$ ceramics having a {1 0 0} orientation could be fabricated at sintering temperatures between 1350 and 1500 °C. The maximum orientation factor reached 99.7% at 10% of template. It was found that texturing improves microwave dielectric low-loss properties, providing a 1.55 times higher Q_f value of 9310 GHz in textured ceramics compared to that of 6005 GHz in non-textured ceramics.

Keywords: Topochemical microcrystal conversion (TMC); Textured ceramics; Templated grain growth (TGG)

1. Introduction

Anisotropically shaped particles having a pseudo-cubic crystal structure, such as the regular-perovskite structure, are of great importance owing to their potential use as template particles in the texturing of grain-oriented ceramics for improving functional properties (e.g., piezoelectricity and microwave dielectricity) of various materials. However, technologically important perovskite-structured materials typically grow as equiaxed particles [1]. Calcium titanate, $CaTiO_3$ (CT), a perovskite-structured dielectric with an orthorhombic crystal phase, is widely used as an end member in microwave dielectrics, such as $CaTiO_3$-(Li,Sm,Nd)TiO_3, $CaTiO_3$-$SmAlO_3$ solid solutions. An interesting application of anisotropically shaped particles, such as particles having a platelike morphology, is their use as templates in the templated grain growth (TGG) [2,3] and reactive templated grain growth (RTGG) [4–7] of textured polycrystalline ceramics, and as templates for the seeded polycrystal conversion (SPC) [8,9] of single crystals. In the TGG method, the initial orientation of the template in the matrix powder achieved by the shear stress results from the anisotropic shape during tape casting, which results in oriented grain growth. Thus, having a compatible anisotropically shaped template is of importance in the TGG method for successfully texturing ceramics.

With reference to the fabrication of grain-oriented CT ceramics, Takeuchi and Tani reported for the first time RTGG-processed textured {1 0 0} CT ceramics using $Ca_3Ti_2O_7$ as a template particle [10]. However, to fabricate the textured CT ceramics having a maximum orientation factor of 93%, a large amount of template material, 74%, was needed. This increased the material cost due to the large fraction of the costly template particles required. In order to reduce the material cost, the TGG method is thought to offer potential to lower the amount of template. However, there are no papers of TGG-processed textured CT ceramics due to the lack of available reports detailing the synthesis of platelike CT particles for template applications.

Recently, we have proposed a new technique for the synthesis of platelike $NaNbO_3$ particles using topochemical

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microcrystal conversion (TMC) [11]. This technique preserves and/or allows the inheritance of the particle shape from an anisotropically shaped precursor to the target compound particle through a topochemical, topotactic and/or pseudomorphic reaction while the chemical composition of the particle is changed.

For synthesis of platelike CT particles, a new processing route for making platelike CT particles was designed using TMC. A layer-structured $CaBi_4Ti_4O_{15}$ (CBIT) was selected as the precursor material, because it is easy to be synthesized in the form of thin platelike particles.

Takeuchi and Tani firstly reported {1 0 0}-texturing of $(Ca_{0.7}Nd_{0.3})_{0.87}TiO_3$ ceramics fabricated by the RTGG method which increased the microwave dielectric low-loss factor Q_f by a factor of 1.1 [12,13]. However, there are no reports of the relationship between microwave dielectric properties and texturing in TGG-processed {1 0 0}-textured CT ceramics.

In this paper, the results of conversion from CBIT to CT particles by TMC are reported from the viewpoint of particle shape inheritance. Subsequently, the fabrication of grain-oriented CT ceramics using TMC-synthesized platelike CT particles as a template by TGG method will be described. Finally, the relationship between microwave dielectric properties and texturing of CT ceramics will be discussed.

2. Experimental procedure

2.1. Synthesis of platelike $CaTiO_3$ particles

A new synthesis route from CBIT to CT particles by TMC has been designed. First, platelike CBIT precursor particles were prepared by molten salt synthesis at 1100 °C for 4 h in accordance with the following equation:

$$CaCO_3 + 2Bi_2O_3 + 4TiO_2 \rightarrow CaBi_4Ti_4O_{15} + CO_2\uparrow$$

In this reaction, $CaCO_3$ (Kojundo Chemical Laboratory, Saitama, Japan, 99%), Bi_2O_3 (Kojundo Chemical Laboratory, Saitama, Japan, 99.99%) and TiO_2 (Kojundo Chemical Laboratory, Saitama, Japan, 99.9%) were used as raw materials, and KCl (Wako Pure Chemical Industries, Osaka, Japan, 99.5%) salt was used as a flux. A mixture of 1:1 by weight of oxide powder to salt was used in the molten salt synthesis. Repeated hot-water washings and decantation were employed to remove the KCl flux during filtration. Using the platelike CBIT precursor particles, the topochemical microcrystal conversion from CBIT to CT was carried out in accordance with the following reaction at 950 °C for 8 h in the molten KCl flux:

$$CaBi_4Ti_4O_{15} + 4CaCO_3 \rightarrow 4CaTiO_3 + 2Bi_2O_3 + 2CO_2\uparrow$$

To remove the KCl flux, repeated hot-water washings and decantation on the filter were performed. Finally, the by-product Bi_2O_3 was removed by a combination of selective dissolution in aqueous 2.5 mol/l of HNO_3 acid and successive filtration. This served to isolate the CT particles. In order to compare the present TMC method with the conventional method with respect to particle shape, CT particles were also synthesized by the conventional flux method according to with the following equation:

$$CaCO_3 + TiO_2 \rightarrow CaTiO_3 + CO_2\uparrow$$

The shape and composition of synthesized particles were characterized by scanning electron microscopy (SEM; S-3600N, Hitachi, Japan) in combination with energy-dispersive X-ray spectrometry (EDX). The crystalline phases were determined by X-ray diffraction analysis (XRD; Rint-TTR, Rigaku, Japan) using CuKα radiation.

2.2. Fabrication of textured $CaTiO_3$ microwave dielectric ceramics

Textured CT ceramics were fabricated by the TGG method using platelike CT particles as a template. The fraction of the CT template selected ranged from 1 to 10 at% for the B-site element. The complementary matrix powder, i.e., equiaxed CT particles having an average grain size of 0.5 μm, was prepared from commercially available CT powder (Kojundo Chemical Laboratory, Saitama, Japan, 99%) by ball-milling in acetone for 24 h with 3 mm-diameter zirconia balls. The template powder and matrix powder were mixed in a solvent (45 vol% ethanol and 55 vol% toluene), binder (6 wt% with respect to total oxide powder; poly(vinyl butyral), Sekisui Chemicals, Japan, BH-3) and plasticizer (6 wt% with respect to total oxide powder; dibutyl phthalate, Wako Pure Chemical Industries, Osaka, Japan) to form a slurry containing 20 vol% total inorganic solids. The slurry was tape-cast using a doctor blade machine (DP-150, Tugawa Seiki, Tokyo, Japan). After drying, a single-layer sheet with a thickness of approximately 80 μm was cut, laminated and hot-pressed at a temperature of 80 °C and pressure of 9.8 MPa for 10 min to form a 2–4 mm-thick green compact. The compacts were further cut into small samples of approximately 5 mm width and 10 mm length. They were heated at 600 °C for 1 h to remove organic substances prior to sintering, and were fired at various temperatures between 1350 and 1550 °C for 1 h in O_2, brought to the maximum temperature at a heating rate of 200 °C/h.

The bulk and theoretical densities of the samples were measured by the Archimedes' method. The theoretical density of CT (4.04 g/cm^3 by JCPDS data No. 042-0423) was used to calculate relative density [14]. The crystalline phases and the degree of texture development were determined by XRD analysis using CuKα radiation. The degree of {1 0 0} orientation of the textured CT ceramics, F, was evaluated by Lotgering's equation [15],

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

where $P = \Sigma I(h\ 0\ 0)\ \Sigma I(h\ k\ l)$, $P_0 = \Sigma I_0(h\ 0\ 0)/\Sigma I_0(h\ k\ l)$, ΣI is the sum of the peak intensities of the XRD pattern for the polished surface of the sintered specimen. ΣI_0 is the summation of the XRD peak intensities of the equiaxed reference powder. Diffraction peaks for values of $2\theta I$ the range 5–70° were used for the calculations.

The dielectric constants, at low frequencies from 1 kHz to 1 MHz, of textured and non-textured specimens were measured

by an impedance analyzer (HP4194A, Agilent, USA). Microwave dielectric properties, at frequencies around 3–5 GHz, of dielectric constant, quality factor Q_f, and temperature coefficient of resonant frequency were measured in the $TE_{0\,1\,1}$ mode by Hakki-Coleman and Kobayashi methods [16,17] using a network analyzer (R3770, Advantest, Japan) and temperature controlled chamber (MC-810, TABAI, Japan). Temperature coefficients of resonant frequency were calculated between 20 and 80 °C.

3. Results and discussion

3.1. Synthesis of platelike $CaTiO_3$ particles

Fig. 1(a) shows a SEM image of CT particles synthesized by the conventional flux method at 1100 °C. The crystalline phase of the particles is orthorhombic perovskite CT, as determined by the XRD pattern shown in Fig. 2(a). Fig. 1(b) shows a SEM image of CBIT particles prepared by the flux method at 1100 °C and they can be fabricated as platelike particles with a width of 3–6 μm and a thickness of less than 0.3 μm. The particles have a layer CBIT structure as determined from the XRD pattern shown in Fig. 2(b), which is assigned by a (JCPDS) powder diffraction file card #52-1640. Fig. 1(c) shows the SEM image of TMC-synthesized CT particles again showing a platelike shape with a width of 3–6 μm and a thickness of less than 0.3 μm. The crystalline phase of the particle is orthorhombic perovskite CT, as determined from the XRD pattern shown in Fig. 2(c), JCPDS powder diffraction file card #042-0423. These data indicated that platelike CT can be synthesized through the TMC reaction, in which CT is formed by the exchange of Ca ions for Bi ions on CBIT with the particle shape preserved and retaining a large shape aspect ratio.

To identify the conversion relationship of the largest developed planes of CBIT and TMC-synthesized CT particles, XRD patterns of particles cast on glass substrates were measured. In this casting method, the largest developed plane of the particles becomes aligned with the glass plane [18]. Fig. 2(b) and (c) is XRD patterns of CBIT and TMC-synthesized CT particles cast on glass substrates, respectively. Larger (0 0 *m*) peaks of CBIT were observed for cast CBIT particles than those given by the JCPDS file, as were larger (2 0 2) and (0 4 0) peaks of CT were observed for cast CT particles. These data show that the largest developed plane of the CBIT and CT is the {0 0 1}. It concluded that during the TMC reaction, the {0 0 1} plane of CBIT has been transformed into the {1 0 0} plane of CT.

To evaluate the atomic conversion ratio from Bi atoms to Ca atoms in the crystalline particles, the EDX profiles of precursor-CBIT particle and TMC-synthesized CT particle as shown in Fig. 3(a) and (b) were measured. Ca, Bi, Ti and O peaks were observed in the EDX profiles. Peaks of Ca and Ti of CT particle are larger than those of precursor-CBIT particle. Table 1 summarizes the results of chemical composition of CBIT and CT. It shows that Ca:Bi:Ti atomic ratio of 1.08:3.91:4:00 in CBIT is in good agreement with chemical formula of $CaBi_4Ti_4O_{15}$. It is clear that the Ca atom replaced 97.1% in the A-site positions, and that 2.2% of Bi atoms remained in the

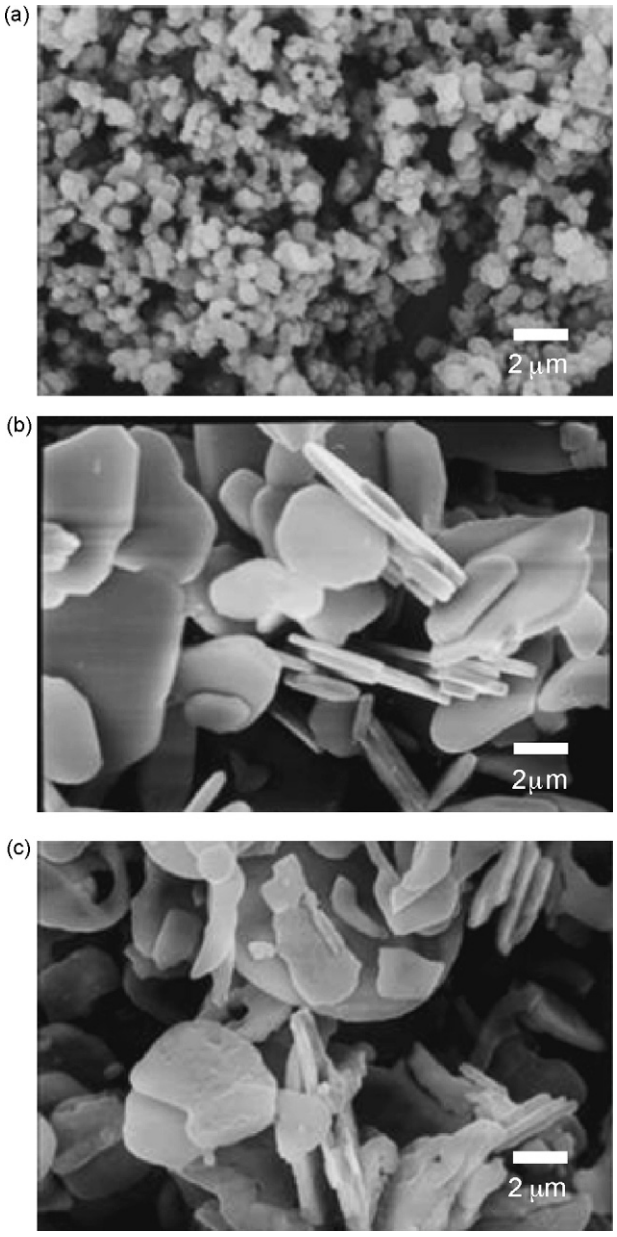

Fig. 1. SEM images. (a) $CaTiO_3$ particle synthesized by conventional flux method at 1100 °C. (b) CBIT precursor particle prepared by molten salt synthesis at 1100 °C. (c) Platelike $CaTiO_3$ particle synthesized by the TMC method from $CaBi_4Ti_4O_{15}$ precursor particle at 950 °C.

crystalline particle. This can be explained using the crystal structures shown in Fig. 4. It is thought that in the layer-structured CBIT crystal, the Bi atoms in the $(Bi_2O_2)^{2+}$ layer can easily diffuse out, whereas the Bi atoms in the pseudo TiO_6-octahedron perovskite block cannot. As a result, Ca atoms cannot easily diffuse in because the three-dimensional atomic arrangement in the pseudo perovskite block is closely packed in the space and associated with high charge density. Thus atoms cannot easily diffuse into and out of the pseudo perovskite block. However, it is assumed that repeated TMC reactions promote the atomic conversion from Bi to Ca. In our future studies, the repeated TMC reactions will be conducted to further reduce the number of Bi atoms in the CT particles.

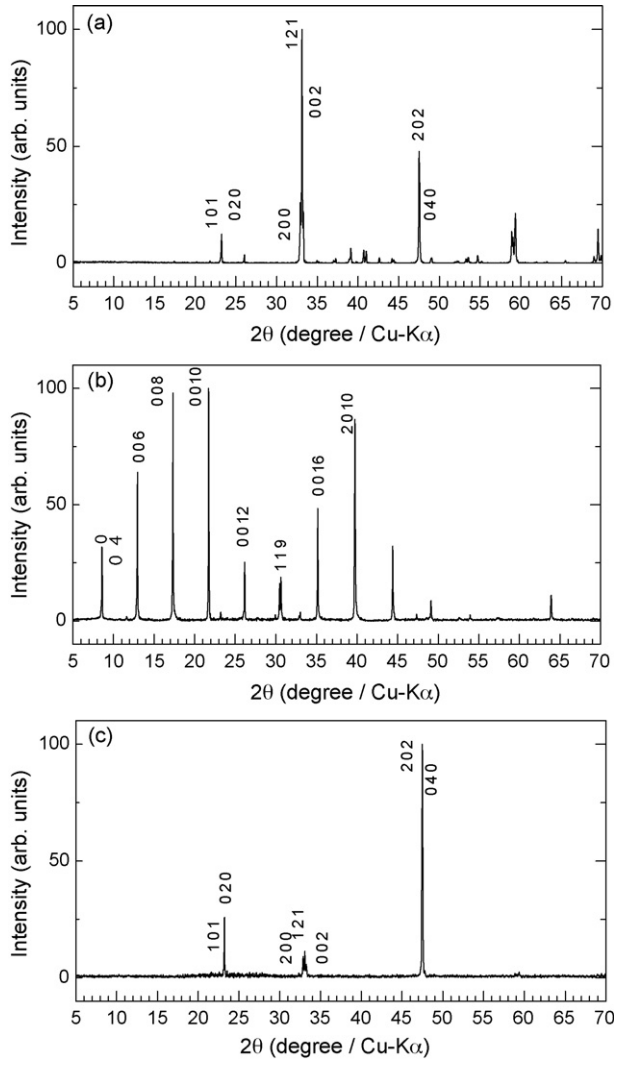

Fig. 2. XRD patterns. (a) $CaTiO_3$ particle synthesized by conventional flux method at 1100 °C. (b) $CaBi_4Ti_4O_{15}$ precursor particle cast on glass substrate prepared by molten salt synthesis at 1100 °C. Major indices are shown by JCPDS powder diffraction file #52-1640. (c) Platelike $CaTiO_3$ particle cast on glass substrate synthesized by the TMC method from $CaBi_4Ti_4O_{15}$ precursor particles at 950 °C. Major indices are shown by JCPDS powder diffraction file #42-0423.

Table 1
Atomic composition of precursor-$CaBi_4Ti_4O_{15}$ and platelike $CaTiO_3$ particle synthesized by the topochemical microcrystal conversion method from precursor particle at 950 °C, as measured by EDX

Particle	$CaBi_4Ti_4O_{15}$		$CaTiO_3$	
Atom	Composition (at%)	Atomic ratio	Composition (at%)	Atomic ratio
Ca	12.04	1.082	48.73	0.971
Bi	43.47	3.908	1.11	0.022
Ti	44.49	4.000	50.16	1.000

3.2. Fabrication of textured $CaTiO_3$ microwave dielectric ceramics

Fig. 5 shows the XRD pattern of a ground surface of ⟨1 0 0⟩ textured CT ceramic sintered at 1450 °C for 1 h in O_2. The fraction of the platelike CT template in the TGG method is 10%. Only 100 and 200 peaks (pseudo-cubic notation) are observed. The calculated Lotgering's factor of the {1 0 0} orientation is as high as 99.7%. The relative density of this sample is 95.7%.

For measurement of microwave dielectric properties, textured ceramics were fabricated using 1 at% CT template at 1500 °C for 1 h in O_2. The reason for selection of the 1 at% template is to decrease microwave dielectric loss, by increasing density, lowering the amount of template and decreasing the impurity Bi atom content. B.D. Silverman and G. Rupprecht reported that low density and higher impurity levels can increase microwave dielectric loss [19,20]. Fig. 6 shows the XRD patterns of ground-side surface (parallel face to ⟨1 0 0⟩ textured axis) and upper face (perpendicular face to ⟨1 0 0⟩ textured axis)) of ⟨1 0 0⟩ textured CT ceramics sintered at 1500 °C for 1 h in O_2 using a 1 at% template. Higher relative densities of 98.9% are observed, compared to 95.7% for the sample using a 10 at% template. However, Lotgering's factor for the {1 0 0} orientation, 87%, is lower than the 99.7% measured for the sample using 10 at% template. This is attributed to the decrease in number oriented grain growth nuclei present with decreasing of amounts of template. The 1 1 0 peak for the side face is larger than that of upper face. This derives from the fact that the sample has one axis orientation, so

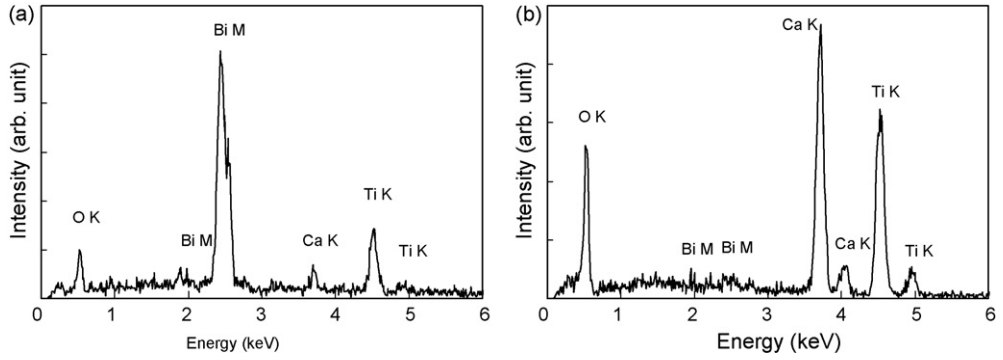

Fig. 3. EDX profile. (a) $CaBi_4Ti_4O_{15}$ precursor particle prepared by molten salt synthesis at 1100 °C. (b) Platelike $CaTiO_3$ particle synthesized by the TMC method from $CaBi_4Ti_4O_{15}$ precursor particles at 950 °C.

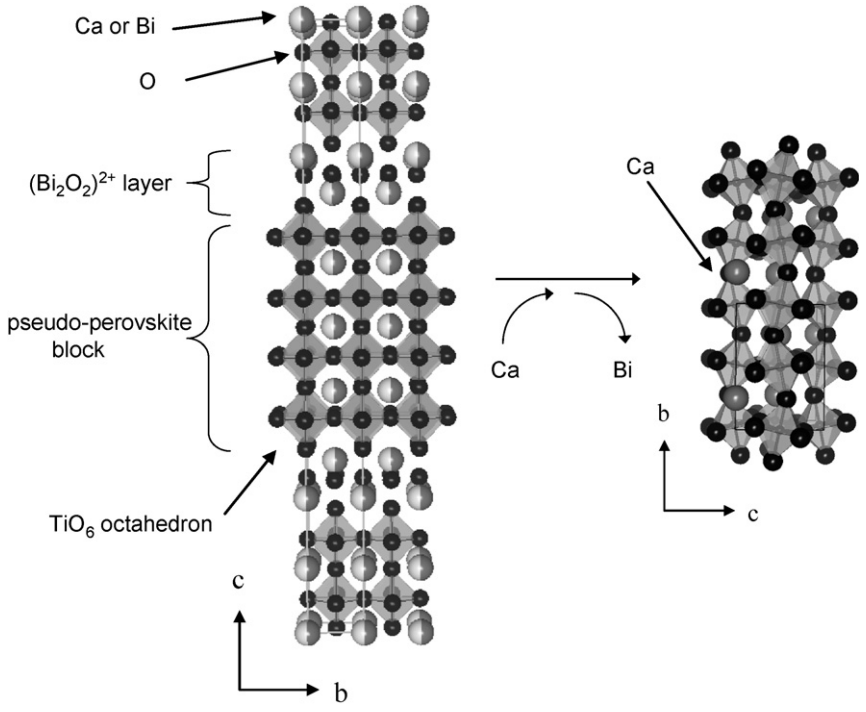

Fig. 4. Crystal structures. (a) Layer-structured $CaBi_4Ti_4O_{15}$. (b) Perovskite-structured $CaTiO_3$.

other crystal faces are randomly rotated around this ⟨1 0 0⟩ axis allowing the 1 1 0 peak on side face to be observed.

Fig. 7 shows the microstructure images of a SEM photograph of non-textured CT ceramics, a BSE image of the upper face of ⟨1 0 0⟩ textured CT ceramics, and a SEM image of the side face of the ⟨1 0 0⟩ textured CT ceramic sintered at 1500 °C for 1 h in O_2 using a 1 at% template. The microstructure of the upper face of ⟨1 0 0⟩ textured CT ceramics is similar to that of non-textured CT ceramics, and side face of ⟨1 0 0⟩ textured CT ceramics has a relatively more aligned "brick wall" like grain pattern than that of side face of the ⟨1 0 0⟩ textured CT ceramics or the face of non-textured ceramics. These results are also due to the single axis orientation, such that other crystal axes are randomly rotated around the ⟨1 0 0⟩ axis. The upper face has a randomly oriented grain pattern.

Table 2 indicates measurement result of microwave dielectric properties between textured and non-textured CT ceramics. The dielectric constants of both samples have almost the same values of 174 and 176. However the Q_f value is enhanced by texturing with a factor of 1.55 from $Q_f = 6055$ GHz in non-textured to 9310 GHz in textured material. Similar trends are also observed

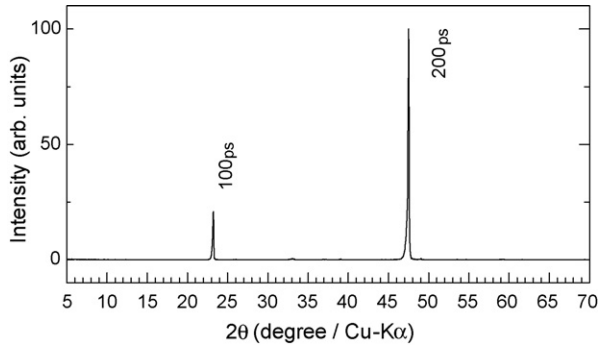

Fig. 5. XRD pattern of the ground surface of $CaTiO_3$ ceramics sintered at 1500 °C for 1 h in O_2 using 10 at% template. Peaks are expressed as pseudo-cubic (ps) notation.

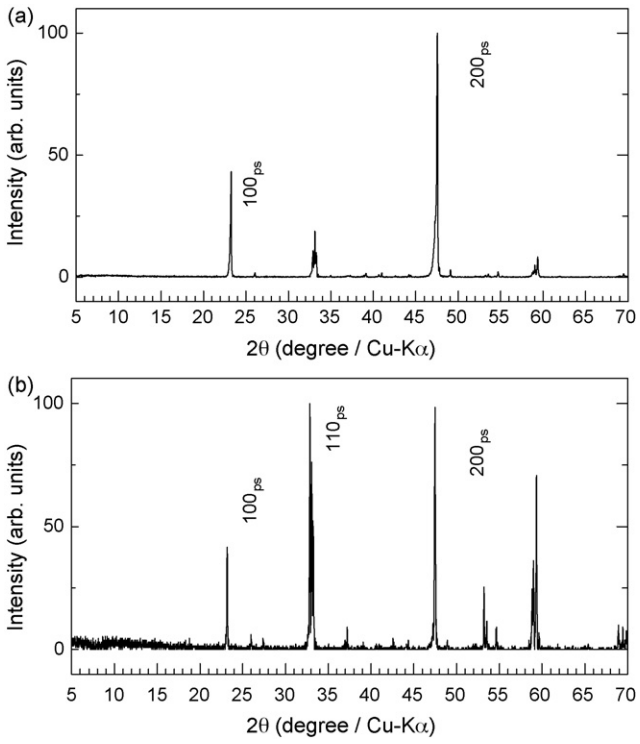

Fig. 6. XRD pattern of (a) side face (b) upper face of the ground surface of $CaTiO_3$ ceramics sintered at 1500 °C for 1 h in O_2 using 1 at% template. Peaks are expressed as pseudo-cubic (ps) notation.

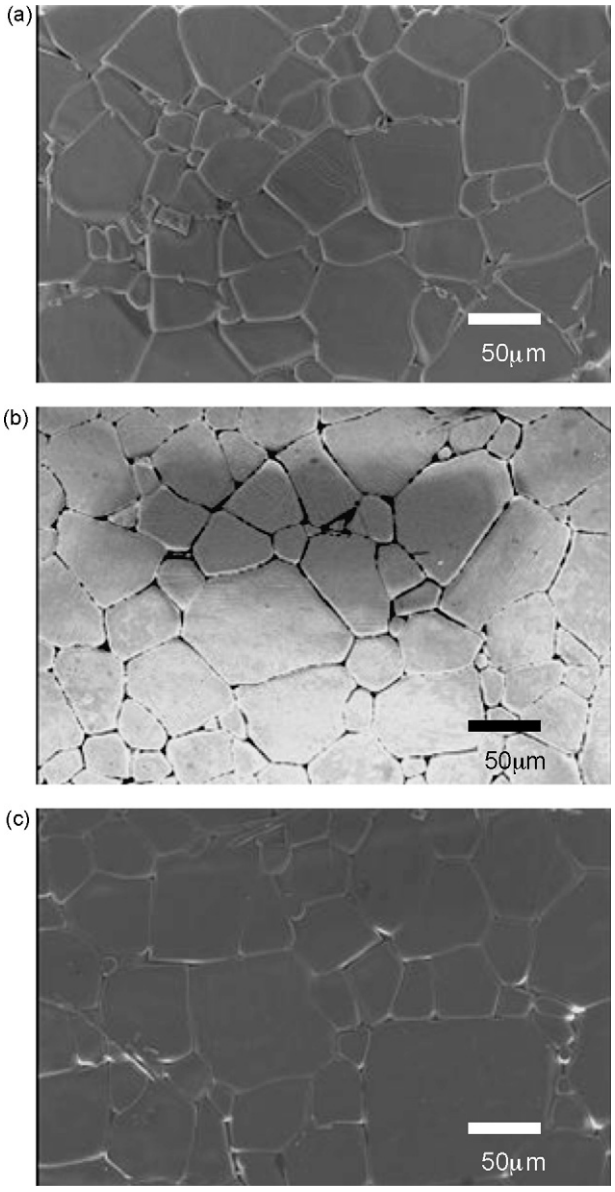

Fig. 7. Microstructure of (a) SEM image of non-textured $CaTiO_3$ ceramics sintered at 1500 °C for 1 h in O_2, (b) BSE image of upper face of ⟨1 0 0⟩ textured $CaTiO_3$ ceramics sintered at 1500 °C for 1 h in O_2 using 1 at% template, (c) SEM image of side face of ⟨1 0 0⟩ textured $CaTiO_3$ ceramics sintered at 1500 °C for 1 h in O_2 using 1 at% template.

Table 2
Comparison of microwave dielectric properties, such as dielectric constant, Q_f value, temperature coefficient of dielectric constant and temperature coefficient of resonant frequency, between non-textured and ⟨1 0 0⟩ textured $CaTiO_3$ ceramics

Sample	Microstructure	ε	Q_f (GHz)	τ_ε (ppm/°C)	τ_f (ppm/°C)	Frequency (GHz)
$CaTiO_3$	Non-texture	174	6005	−1442	824	3.41
$CaTiO_3$	⟨1 0 0⟩ texture	176	9310	−1535	771	4.53

at the temperature range from −40 to 80 °C. Fig. 8 shows the measurement results of temperature dependencies of microwave dielectric constant in Fig. 8(a) and Q_f value in Fig. 8(b). In this temperature range, the dielectric constants are not significantly different between non-textured and textured ceramics. The dielectric constants gradually increase with decreasing temperature, according to the Curie–Weiss law. Since CT has a transition from paraelectric phase to quantum paraelectric phase at a lower temperature of 12 K. The difference of Q_f values between non-textured and textured ceramics increase with increasing temperature.

The reason underlying the larger Q_f value of the textured ceramics than for the non-textured ceramics is thought to be a lower grain boundary scattering loss. Rupprecht reported [20], that in microwave ceramics, the origins of dielectric loss are grain boundary scattering, impurity damping loss, imperfection damping loss (lattice defect loss) and intrinsic lattice damping loss. Grain boundary scattering loss depends on grain size and grain orientation. In this experiment, the same matrix powder and same template particle are used when fabricating both non-textured and textured ceramics, so these two samples have the same amount of impurity Bi atoms. Both samples were sintered under the same sintering condition, so they have similar grain sizes and patterns as shown in Fig. 7(a) and (b). Using the same powder source and the same sintering condition, both samples should have a similar amount of lattice defects, since the generation of lattice defect is strongly dependent on sintering temperature and the rate of temperature rise and fall. The intrinsic lattice damping losses are the same in non-textured and textured ceramics. As a result, the only difference between textured and non-textured ceramics is the degree of grain

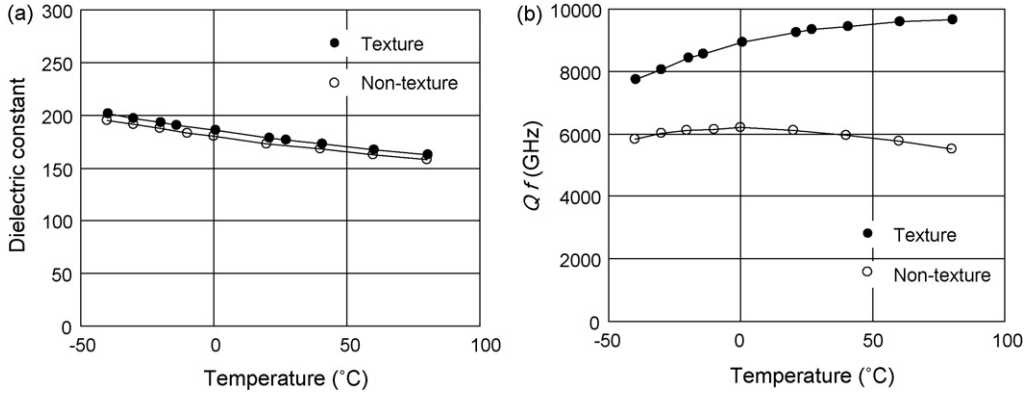

Fig. 8. Temperature dependency of microwave properties (a) dielectric constant, and (b) Q_f value of ⟨1 0 0⟩ textured $CaTiO_3$ ceramics sintered at 1500 °C for 1 h in O_2 using 1 at% template under $TE_{0\,1\,1}$ mode.

orientation. In $TE_{0\ 1\ 1}$ mode, an electric field direction is perpendicular to ⟨1 0 0⟩ textured axis, so electric field in textured ceramics penetrate more uniform grain boundary than that in non-textured ceramics. This leads to a smaller grain boundary scattering loss in the textured ceramics than that in non-textured ceramics.

It should be noted that this mechanism of lowering of the Q_f value by texturing is independent of composition. Our future studies will try to fabricate other microwave dielectric textured ceramics to support this assertion.

4. Conclusions

A new synthesis route for fabricating platelike CT particles with an orthorhombic perovskite structure by the topochemical microcrystal conversion (TMC) method from platelike precursor particles of layer-structured CBIT has been developed. Using TMC, we are able to synthesize platelike CT particles whose shape preserved the that of the precursor particles with a thickness less than 0.3 μm and a width of 3–6 μm. X-ray diffraction analysis revealed that in the TMC reaction, the crystallographic {0 0 1} plane of CBIT is converted to the {1 0 0} plane of CT.

Using these platelike CT particles as a template in the templated grain growth method, {1 0 0} grain-oriented CT ceramics having a {1 0 0} orientation degree (Lotgering's factor) higher than 87% could be fabricated at sintering temperatures between 1350 °C and 1500 °C. The relative densities of the resultant ceramics were over 95%. The maximum orientation factor reached was as high as 99.7%. Texturing improved the Q_f value by a factor of 1.55 through a decrease of scattering loss at grain boundaries.

The proposed TMC method is thought to be a suitable method of fabricating platelike particles for the template of textured ceramics with regular-perovskite-structured materials, and for fabricating low loss microwave dielectric ceramics.

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