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Synthesis of polycrystalline platelike $NaNbO_3$ particles by the topochemical micro-crystal conversion from $K_4Nb_6O_{17}$ and fabrication of grain-oriented $(K_{0.5}Na_{0.5})NbO_3$ ceramics

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Abstract Topochemical microcrystal conversion (TMC) method is a powerful tool to synthesize platelike microcrystal particles with a regular-perovskite crystal structure, which is difficult to be fabricated by conventional flux techniques. By using the TMC method, polycrystalline rectangular-platelike $NaNbO_3$ particles with a orthorhombic perovskite structure were able to be synthesized from platelike precursor particles of layer-structured $K_4Nb_6O_{17}$ at 1000°C in molten NaCl-salt. The TMC-synthesized $NaNbO_3$ particles preserved the shape of precursor particles, and had a thickness of about 1 micron and a width of 5-10 microns. However TMC-synthesized platelike $NaNbO_3$ particles had a polycrystalline morphology having a preferred pseudo-cubic {100} orientation. Oriented particulate layer X-ray diffraction (OPL-XRD) analysis revealed that, during the TMC reaction, the crystallographic {010} plane of $K_4Nb_6O_{17}$ is converted to the most of {001} plane of polycrystalline $NaNbO_3$ particles in spite of polycrystalline morphology. Using the polycrystalline platelike $NaNbO_3$ particles as a template in the reactive templated grain growth method (RTGG), {001} grain-oriented $(K_{0.5}Na_{0.5})NbO_3$—1 mol% CuO ceramics having a {001} orientation degree (Logering's factor) of 45% 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 RTGG process. The availability of polycrystalline particles will give a new design of synthesizing templates for texturing of various kinds of perovskite crystal-structured ceramics.

Keywords Platelike $NaNbO_3$ particle · Polycrystalline particle · Topochemical Micro-crystal Conversion (TMC) · Pseudomorph · Topotaxy · Textured ceramics · Template · Templated Grain Growth (TGG) · Reactive Templated Grain Growth (RTGG)

1 Introduction

Nb-perovskite structured piezoelectric ceramics have attracted much attentions due to it relatively high piezoelectric performance in lead-free piezoelectric family, recently. However, their piezoelectric constants are not enough value to catch up with the piezoelectric performance of $Pb(Zr,Ti)O_3$ family as the form of non-textured ceramics [1]. Therefore, to replace the Pb-contained piezoceramics family by using lead-free piezoceramics, it has been thought that some techniques to enhance the piezoelectric performance must be needed.

Among the enhancement technologies in ceramics, texturing of the polycrystalline ceramics, such as templated grain growth (TGG) [2, 3], reactive templated grain growth (RTGG) [4, 5], and seeded polycrystal conversion (SPC) [6, 7], are of great importance due to its large enhancement of piezoelectric performance. However, regular-perovskite structured materials typically grow as cubic particles [1], and it is difficult to synthesized platelike particles using

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conventional methods such as flux method, hydrothermal method and so on.

Recently, we proposed a new technique for the synthesis of platelike $NaNbO_3$ (NN) particles using our developed topochemical micro-crystal conversion (TMC) method [8, 9]. This technique preserves and/or inherits the particle shape from an anisotropically shaped precursor (platelike $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ particles) to the objective compound particle (platelike NN) through a topochemical, topotactic and/or pseudomorphic reaction while the chemical composition of the particle is varied. For platelike $KNbO_3$ particles, we reported the fabrication result of polycrystalline platelike $KNbO_3$ micro-particles by TMC reaction from $K_4Nb_6O_{17}$ to $KNbO_3$. [10]

From the synthesis design, there is a possibility of synthesizing the micro-meter-sized platelike NN particles having the orthorhombic perovskite crystal structure, by using TMC reaction from precursor K4N6 to NN. However, there is no report of TMC reaction from K4N6 to NN.

In this paper, first, the results of conversion from $K_4Nb_6O_{17}$ to $NaNbO_3$ particles by the TMC method from the viewpoint of particle shape inheritance were reported. Then, 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 was described. Finally, the discussion of the conversion mechanism from $K_4Nb_6O_{17}$ to $NaNbO_3$ particles in the TMC reaction will be presented.

2 Experimental procedure

2.1 Synthesis of platelike $KNbO_3$ particles

First the platelike $K_4Nb_6O_{17}$ (K4N6) to $NaNbO_3$ (NN) particles by the TMC method was designed. First, platelike $K_4Nb_6O_{17}$ precursor particles were prepared by molten salt synthesis at 1050°C for 2 h according to the following equation:

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

The raw materials of K_2CO_3 (Aldrich, Milwaukee, WI, USA, 99.99%) and Nb_2O_5 (Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan, 99.99%) were used in this synthesis reaction, and KCl (Wako Pure Chemical Industries, Ltd., Osaka, Japan, 99.5%) salt was used as a flux. In the molten salt synthesis, a mixture of 1:1 by weight of objective oxide powder of final product to salt was used. To remove the NaCl flux, repeated hot-water washing and decantation was employed during filtration. Next, using platelike K4N6 precursor particles, the topochemical micro-crystal conversion from K4N6 to NN was carried out according to the following reaction scheme at 1000°C for 2 h in a molten NaCl flux:

$$K_4Nb_6O_{17} + 3(1 + x)\ Na_2CO_3 \rightarrow 6\ NaNbO_3 + 3x\ Na_2CO_3 + 2\ K_2CO_3 + 2CO_2 \uparrow,$$

where x was selected as 0.2 from the result of our previous study. [10] To remove both the NaCl flux and the excess amount of Na_2CO_3, repeated hot-water washing and decantation on the filter was performed. Finally, to isolate synthesized $NaNbO_3$ particles, successive filtration were applied. For the comparison between this TMC method and a conventional flux method with respect to particle shape, we synthesized $NaNbO_3$ particles by the conventional flux method at 1000°C for 2 h in a molten NaCl flux according to the following equation:

$$Na_2CO_3 + Nb_2O_5 \rightarrow 2\ NaNbO_3 + CO_2 \uparrow .$$

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) and X-ray diffraction analysis (XRD; Rint-TTR, Rigaku, Japan) using CuK_α radiation. The crystalline phases were determined by XRD. 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) [11].

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

We fabricated 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 [5], by the reactive templated grain growth (RTGG) method with the use of TMC-synthesized polycrystalline platelike $NaNbO_3$ particles as a template. The fraction of the $NaNbO_3$ template was selected as 2 at% for the B-site element of Nb according to the following equation:

$$0.5\ KNbO_3(\text{matrix}) + 0.5\ \{0.98\ NaNbO_3(\text{matrix}) + 0.02\ NaNbO_3(\text{template})\} + 0.01\ CuO \rightarrow (K_{0.5}Na_{0.5})NbO_3 - 0.01CuO(\text{ceramics}).$$

The complementary matrix powder, i.e., equiaxed $KNbO_3$ and $NaNbO_3$ particles having an average grain size of 0.5 microns, were prepared from raw powders of K_2CO_3 (Aldrich, Milwaukee, WI, USA, 99.99%), Na_2CO_3 (Rare metallic, Tokyo, Japan, 99.99%), and Nb_2O_5 (Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan,

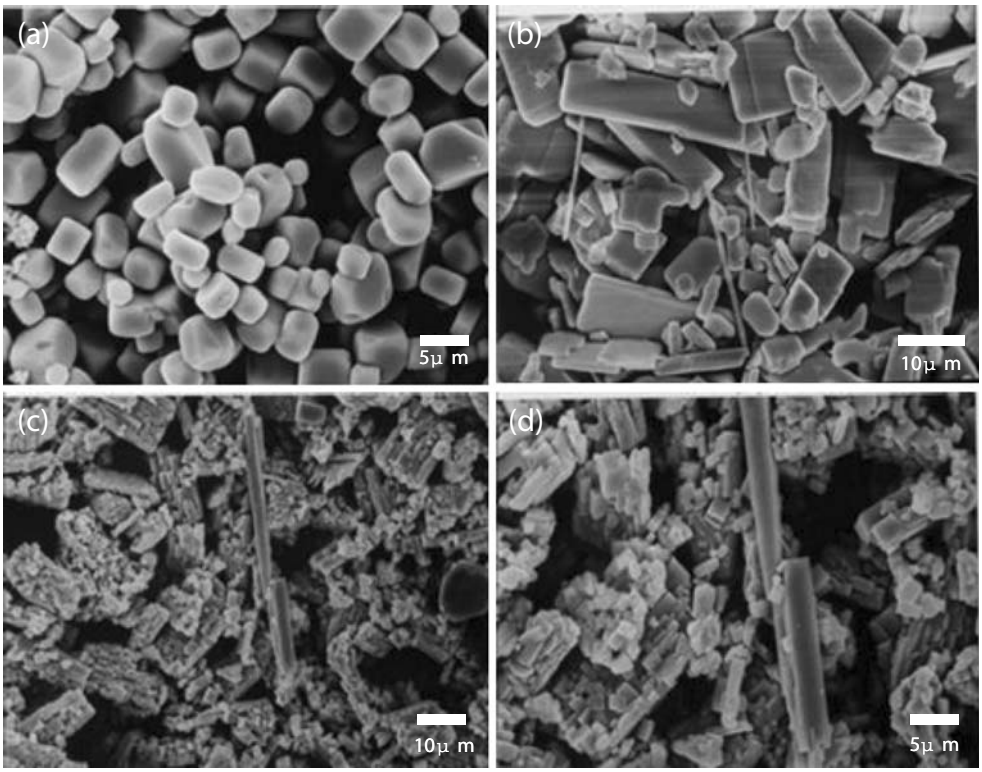

Fig. 1 SEM images. (**a**) $NaNbO_3$ particles synthesized by the conventional flux method at 1000°C for 2 h. (**b**) $K_4Nb_6O_{17}$ precursor particles prepared by molten salt synthesis at 1050°C for 2 h. (**c**) and (**d**) Platelike $NaNbO_3$ particles synthesized by the topochemical micro-crystal conversion method from $K_4Nb_6O_{17}$ precursor particles at 1000°C for 2 h

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., Saitama, Japan, 99.99%) powder was used as the sintering aid.

We mixed the template particles and matrix powders in a solvent (45 vol.% ethanol and 55 vol.% toluene), binder (poly-vinyl butyral, Sekisui Chemical, Japan, BH-3) and plasticizer (di-butyl phthalate, Wako Pure Chemical Industries, Ltd., Osaka, Japan) 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 microns 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°C and 1175°C for 1 h in O_2 atmosphere, brought to temperature at a heating rate of 200°C/h.

By the Archimedean method, apparent densities of the samples were measured. To calculate the relative density, the measured XRD density of non-textured KNN—1%CuO ceramics (4.506 g/cm^3) [9] was used. The crystalline phases and the degree of texture development were determined by XRD analysis using CuK$_\alpha$ radiation. Lotgering's equation [12] was applied to evaluate F value of the degree of pseudo-cubic {001} orientation of the textured KNN—1% CuO ceramics,

$$F = (P - P_0)/(1 - P_0),$$

where P=sum I(00 h)/sum I(hkl), P_0=sum I_0(00 h)/sum I_0(hkl), 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 2θ=5° to 70° were used for the calculations.

3 Results and discussion

3.1 Synthesis of platelike NN particles

Figure 1(a) shows an SEM image of NN particles synthesized by the conventional flux method at 1000°C. Only cube-shaped NN particles were observed. The crystalline phase of these particles is an orthorhombic perovskite $NaNbO_3$ structure, as determined by the XRD pattern shown in Fig. 2(a). Figure 1(b) shows an SEM image of K4N6 particles prepared by the flux method at 1050°C. K4N6 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 K4N6 structure assigned by the XRD pattern shown in

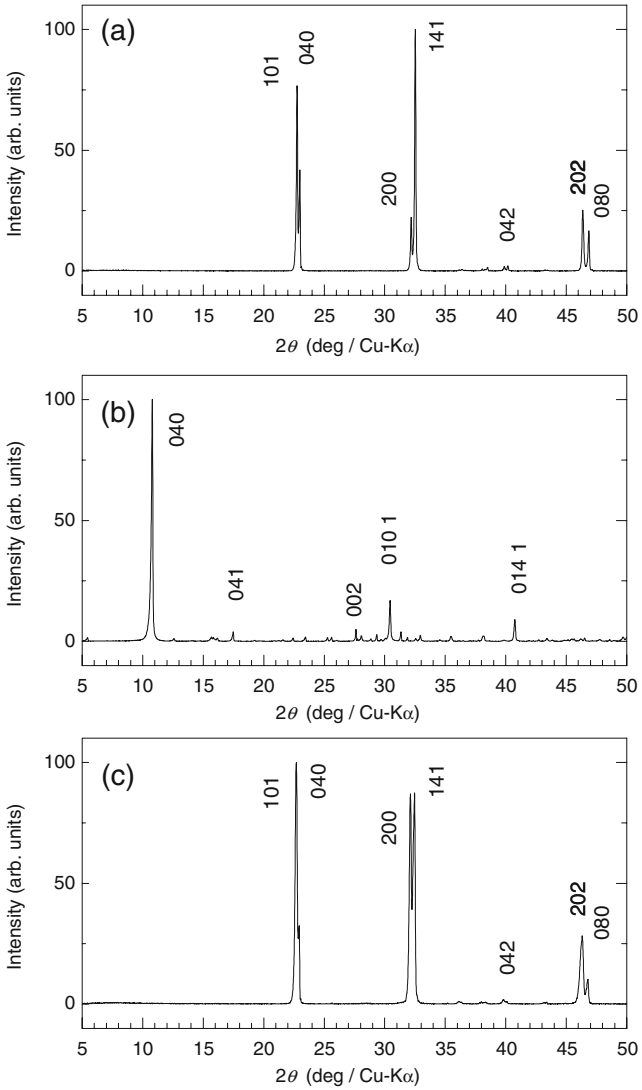

Fig. 2 X-ray diffraction patterns. (**a**) $NaNbO_3$ particles synthesized by the conventional flux method at 1000°C for 2 h. Peaks are indexed by JCPDS powder diffraction file # 33-1270. (**b**) $K_4Nb_6O_{17}$ precursor particles prepared by molten salt synthesis at 1050°C for 2 h. Peaks are indexed by JCPDS powder diffraction file #76-0977. Major Miller indices are shown. (**c**) Platelike $NaNbO_3$ particles synthesized by the topochemical micro-crystal conversion method from $K_4Nb_6O_{17}$ precursor particles at 1000°C for 2 h

Fig. 2(b), which is identified by JCPDS powder diffraction file card No.76-0977.

Figure 1(c) shows a SEM image of TMC-synthesized NN particles at the reaction condition of x=0.2. 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 K4N6 precursor's shape without breaking into individual smaller particles. The crystalline phase of the TMC-synthesized platelike particles is an orthorhombic perovskite structured NN, as determined by the XRD pattern shown in Fig. 2(c), which is identified by JCPDS powder diffraction file card No.33-1270.

These data mean that polycrystalline platelike NN particles having single perovskite crystal phase can be synthesized through the TMC reaction under the reaction condition of x=0.2, in which NN formed by Na ion diffusing into and K ion diffusing out K4N6 crystal while preserving particle outer-shape and a largest developed plane.

To identify the largest developed planes of K4N6 and TMC-synthesized NN particles, we measured XRD patterns of particles that were cast on glass substrates, which is called oriented particulate layer (OPL) X-ray diffraction measurement technique [11]. In this casting method (OPL-XRD method), the largest developed plane of the particles is easily aligned with the glass plane. From OPL-XRD results, It indicated that the developed plane of K4N6 is the {010} plane, and the major developed plane of TMC-synthesized NN with polycrystalline morphology is the {001} plane. This means that the grains in polycrystalline particle statistically preferably aligned or oriented along <001> axis in a pseudo-cubic notation in each particle. It suggests that, during the TMC reaction, the largest {010} plane of single crystalline K4N6 is kept its shape and converted into the preferred pseudo-cubic {001} plane of polycrystalline NN particles without breaking the shape of platelike particle.

To evaluate the atomic ratio of Na: Nb at the end of the TMC reaction in the particles, the XRD and EDX profiles of both K4N6 and TMC-synthesized NN particles were measured. Figure 3 shows comparison of XRD measurement profiles among $KNbO_3$, $NaNbO_3$ and TMC-synthesized platelike $NaNbO_3$ particles synthesized at 1000°C for

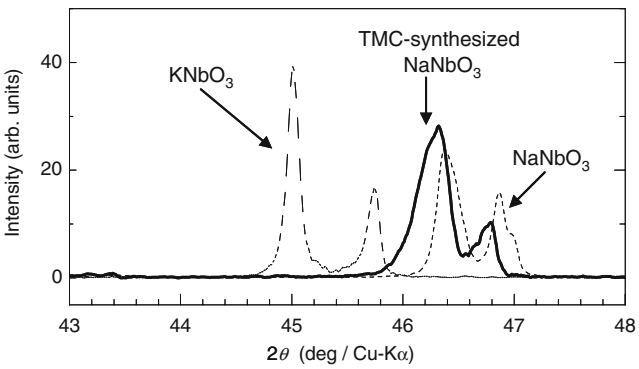

Fig. 3 Comparison of XRD patterns among $KNbO_3$, $NaNbO_3$ and Platelike $NaNbO_3$ particles. $KNbO_3$ particles were synthesized by the conventional flux method at 950°C for 2 h. $NaNbO_3$ particles were synthesized by the conventional flux method at 1000°C for 2 h. Platelike $NaNbO_3$ particles synthesized by the topochemical micro-crystal conversion method from $K_4Nb_6O_{17}$ precursor particles at 1000°C for 2 h

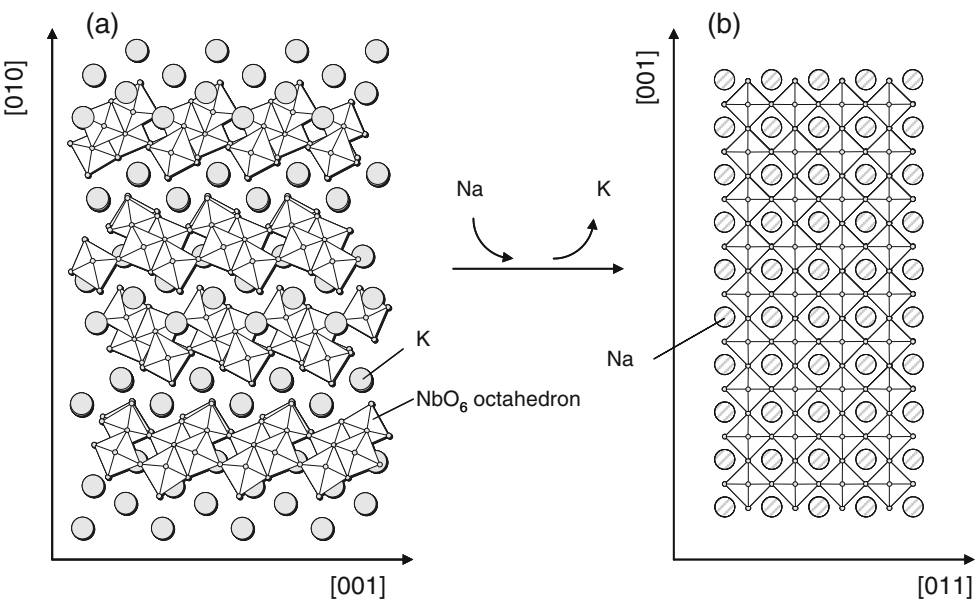

Fig. 4 Schematic crystal structure and reaction scheme. (**a**) Layer-structured $K_4Nb_6O_{17}$ along the [100] direction, (**b**) Perovskite-structured $NaNbO_3$

2 h. It is clear that the 002 and 200 peaks around 45°, which are assigned by pseudo-cubic notation, of TMC-synthesized NN are shift to higher angle positions where they are very close to the position of the peaks of pure $NaNbO_3$. From Vegard rule of XRD pattern, the K:Na ratio was calculated as about 95%: 5%. Also, EDX profile measurement of the same powder gave the K:Na atomic ratio of 92.5%: 7.5%. These data indicates an atomic conversion from K to Na is possible by TMC reaction from K4N6 to NN. The obtained NN has the composition of $(Na_{0.925}K_{0.075})NbO_3$. And it is thought that, to achieve a perfect atomic conversion from K to Na, repeated TMC reactions would be needed.

From the crystal structures shown in Fig. 4, it is understood that a reason of formation of polycrystalline NN particles having preferred {001} orientation during TMC reaction from K4N6 to NN. In the TMC reaction, {010} planes of K4N6 are converted to preferred {001} planes of NN. The structure of K4N6 could be characterized as a stacking of Nb_6O_{17} sheets (or layers) consisting 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 [001] direction, and connect with sharing corners along the [100] direction. In the perovskite NN crystal, NbO_6 octahedron units connect with sharing corners along the [001], [010] and [001] directions. When TMC reaction occurs in K4N6 crystal, Na-ions must be needed to diffuse inside the K4N6 crystal, probably

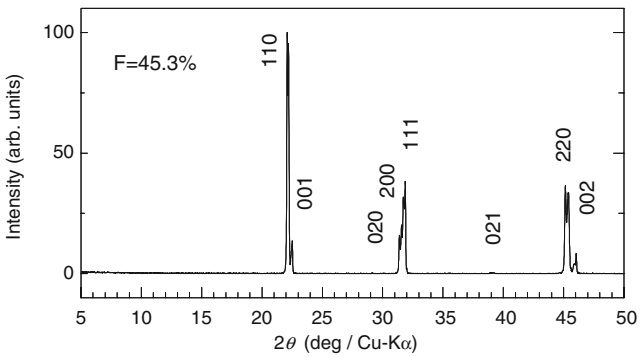

Fig. 5 XRD profiles of grinded surface of textured $(K_{0.5}Na_{0.5})NbO_3$—1 mol% CuO ceramics sintered at 1175°C for 1 h using 2% of TMC-synthesized NN template. The XRD profiles are assigned using orthorhombic Miller indices. *F* is the degree of pseudo-cubic {001} orientation

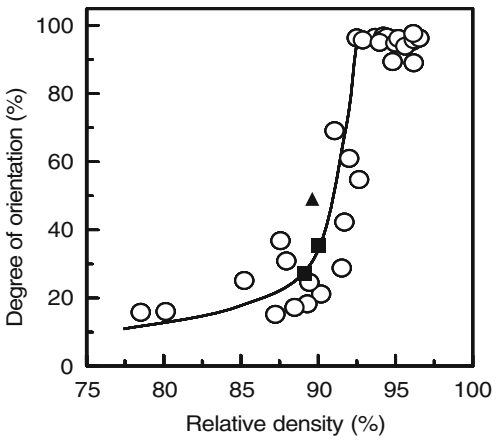

Fig. 6 Relationship between degree of pseudo-cubic {001} orientation of textured $(K_{0.5}Na_{0.5})NbO_3$—1 mol% CuO ceramics sintered at 1000°C to 1175°C in O_2 atmosphere and relative density. *Empty circles* and *filled squares* previously reported our data [9,10], *filled triangle* this work

through along a plane of sheet direction, because K4N6 has a K-atom composition deficient compared to that of NN. During conversion, the bonds of edge-sharing NbO_6 octahedra in the Nb_6O_{17} layer along the [001] direction must be separated. This bond breaking would make the NbO_6 octahedra rotate. Subsequently, the bonds of corner-sharing NbO_6 octahedra in the Nb_6O_{17} layer, will re-connect. These new-bond formations occurs simultaneously as a diffusion of Na atoms into the Nb_6O_{17} layer occurs. Altogether, they are complex reactions of bond breaking of the edge-sharing NbO_6, new bond formation of corner sharing NbO_6 associated with a rotation of the octahedron, and creating a new generation of corner-sharing bonds of NbO_6 octahedron units between the layers. They are very complicated to be perfectly understood. As a result, through these complicated conversion reactions from layer structured K4N6 to perovskite structured NN, it gave the polycrystalline structured platelike NN particles with a grain size of about 0.5 μm

Despite the TMC-synthesized NN particles have polycrystalline morphology, however, it has preferred {001} oriented plane in each particle. Therefore, the TMC-synthesized particles have a possibility to act as template in templated grain growth process. Next section, the result of fabrication of textured ceramics using the TMC-synthesized particles is reported.

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

Figure 5 shows the XRD patterns of the surface of a grinded $(K_{0.5}Na_{0.5})NbO_3$—1 mol% CuO ceramic, sintered at 1175°C for 1 h in O_2. The fraction of NN template in the RTGG method is 2%. Larger peaks of (110), (001), (220) and (002), which are re-indexed as {001} 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 {001} orientation in pseudo-cubic notatin is 45.3%. This means that polycrystalline platelike particle is act as template for texturing ceramics.

Figure 6 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. We reported in the previous paper that in the region between 77–90% of relative density, the degree of orientation increase gradually up to only 30%, but continue rapidly to increase when the density pass over 90%. The samples prepared according to this paper, is plotted as a closed triangle with the solid curve which is based on previous experiments [9, 10]. This means that one of the reason behind obtaining only 45.3% {001} orientation is because its low density of 89.1% which is because of inhibition of densification during sintering by the large TMC-synthesized NN templates.

In 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 NN template particles.

4 Conclusions

A new synthesis route for fabricating platelike NN particles with an orthorhombic perovskite structure was designed by a TMC method using a particle precursor consisting of a layered structure of K4N6. By TMC method, polycrystalline rectangular-platelike NN particles could be synthesized, whose outer-shape copied the shape of the precursor particles, and had a thickness of about 0.5-1 micron, a width of 5–10 μm, and a length of 20–40 μm. OPL-XRD technique revealed that the crystallographic {010} plane of K4N6 is converted into a dominating {001} plane of polycrystalline NN particles in spite of polycrystalline morphology. Using the polycrystalline platelike NN particles as a template in the RTGG method, {001} grain-oriented $(K_{0.5}Na_{0.5})NbO_3$—1 mol% CuO ceramics having a pseudo-cubic {001} orientation degree (Logering's factor) of 45.3% could be fabricated. This indicates that the polycrystalline particles can be act as template in the RTGG process. This new method of fabricating textured ceramics presented here, will open up new directions of synthesizing template particles for further variations of perovskite structured ceramics.

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