Grain orientation of Nd-modified bismuth titanate ceramics by forming at low magnetic field

Yuya KOMATSU, Tetsuo UCHIKOSHI, Hidenobu ITOH and Junichi TAKAHASHI

Faculty of Engineering, Hokkaido University, Kita-13 Nishi-8, Kita-ku, Sapporo 060–8628, Japan
Department of Materials Science, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090–8507, Japan

Grain-oriented Nd-modified bismuth titanate (BNIT) ceramics with the a-b-plane perpendicular to the direction of magnetic field (MF) were successfully fabricated by applying MF-assisted forming at lower field strengths. A BNIT powder, in which 25% of the Bi4+ site were substituted with Nd3+, was synthesized by coprecipitation in an alkaline solution and successive calcination at 600°C. Green compacts of the BNIT powder were formed by applying various MF strengths (2–12 T) during slip casting and then sintered at 900 and 1000°C for different times. The cation substitution with Nd3+ large anisotropy in its ferroelectric property.

1. Introduction

Ferroelectric Aurivillius compounds (BLSFs) have a unique crystal structure which is composed of bismuth oxide based layers, (Bi2O3)2+−, interleaved with pseudo-perovskite-type layers, (A+−B−O6)m−1)2− where A and B are large and small cations, respectively, and m is an integer showing the number of the octahedral BO6 unit constituting the pseudo-perovskite-type layers. Most of the compounds have been promising candidate materials for high temperature piezoelectric applications, because they are Pb-free and have high Curie temperatures. Among the Aurivillius family, Bi4Ti3O12 (BIT) with magnetic-

2. Experimental procedure

Fixed amounts of chemically pure Bi2O3 and Nd2O3 (both from Kojundo Co., Japan) were dissolved in an aqueous HNO3 solution, to which a given amount of Ti-tetraisopropoxide was added as a titanate source. The mixture was aged for 1 day and then transferred into a 37°C water bath for 24 h. Afterward, the aged mixture was slowly evaporated at 85°C for 24 h to synthesize the 

Corresponding author: H. Itoh; E-mail: itoh@catal.chem.kitami-it.ac.jp

©2014 The Ceramic Society of Japan. All rights reserved.

Key-words : Bi4Ti3O12, Cation substitution with Nd3+, Magnetic-field-assisted forming, Grain orientation, Preferential grain growth
added. A transparent HNO$_3$ solution containing Bi$^{5+}$, Nd$^{3+}$, and Tl$^{+}$ cations was then continuously poured into an aqueous ammonia solution, producing the stoichiometric coprecipitation of the metal cations as solid particles. The coprecipitates were washed with distilled water, dried at 120°C, and calcined at 600°C for 4 h. The Bi content in the coprecipitates was adjusted to 4 mol % excess for all samples to suppress the compositional deviation induced by Bi vaporization and to promote effectively the densification of a sample during sintering. Thus, calcined BNIT powders in which 12.5 mol % or 25.0 mol % of the Bi component were substituted with Nd were obtained for subsequent forming and sintering processes. Hereafter, these samples are called 12.5Nd-BIT and 25Nd-BIT samples, respectively, in this study. For comparison, a 0Nd-BIT powder, without Nd-substitution, was also prepared. The magnetic properties of calcined powders were evaluated by vibrating sample magnetometer (VSM) at room temperature.

For slurry preparation, the calcined BNIT powder (5 g) was dispersed in 10 ml of distilled water with 0.125 g of ammonium polyacrylate (ALON-A-6114, Teagosei Chem.) as a dispersant, which was then classified into two portions by sedimentation in the suspended solution. A supernatant portion of the suspension that contained very fine BNIT particles was used in the following slip casting process. The slurry thus prepared was poured into a plastic cylindrical mold which was placed on a sheet of membrane filter (opening of 0.2 μm) set on a porous aluminia support. Vertical MF ranging from 2 to 12 T induced by a superconducting magnet (JMTD-12T100NC5, Japan Superconductor Technology Inc., Hyogo, Japan) was applied to the slurry during slip casting. The suspension was consolidated to a green cake during the slip casting for 12–14 h (overnight) in the MF. The consolidated green cakes were fully dried in air and the dried cakes were sintered at 900 and 1000°C for different times.

The crystal phase and grain (particle) orientation were examined by X-ray diffraction (XRD) analysis (Rigaku, RINT 2200). The degree of grain (particle) orientation was estimated by Lotgering factor, $L_{t} = (P − P_{0})/(1 − P_{0})$ where $P = ΣI(\text{selected peak})/ΣI(\text{bkl})$ and $P_{0} = P$ obtained for a randomly oriented sample. In this study, the values of the denominator and numerator of $P$ are the sum of intensities for all diffraction peaks ranging from 2θ = 10 to 60°, and that for the diffraction peaks of (200), (020), (220), and (111), respectively. Density was measured by the Archimedes method and the microstructure was observed for the polished and thermally-etched samples with Scanning Electron Microscope (SEM, JEOL JSM-6300F). Dielectric permittivity ($\varepsilon_r$) was measured with a digital LCR meter (HP-4274A, at 10 kHz) in a temperature range of 50–700°C.

3. Results

3.1 Characterization of synthesized BNIT powder

Figure 1 shows the XRD pattern of a 25Nd-BIT powder calcined at 600°C. The synthesized powder was identified with the single phase Nd-modified BIT. All peaks are assigned as having the orthorhombic symmetry with the longer c-axis. A SEM image of the calcined BNIT powder in Fig. 2 indicated that coprecipitation and calcination at 600°C produced a very fine powder ($S_{s} = 18.7 \text{ m}^2/\text{g})$ with an equiaxial particle shape. Figure 3 shows the magnetic property change of the calcined powders with the amount of Nd$^{3+}$ incorporated. The Nd$^{3+}$ substitution obviously changes the magnetic property of pure BIT from diamagnetic to paramagnetic. It is also clear that the magnetization value gradually increased with increasing amount of Nd$^{3+}$ incorporated. Thus, the cation substitution with Nd$^{3+}$ for the Bi$^{3+}$-site provided a weak paramagnetic property for BIT. In the following examination, the calcined 25Nd-BIT powder having a larger magnetization character was used.

3.2 Fabrication of grain-oriented 25Nd-BIT ceramics by forming at lower MFs

Figure 4 shows the peak intensity changes of the XRD patterns with the strength of MF applied during slip casting for 25Nd-BIT samples sintered at 1000°C for 4 h. The sample formed at 0 T shows a maximum XRD intensity for the (117) peak, which corresponds to the reference data of random orientation. As the MF increased, the peak intensities of (111), (200), (020), and (220) relative to (117) gradually increased. The similar changes in the diffraction peak intensities were reported in other studies on the fabrication of BIT ceramics using a very strong MF-assisted
The increasing XRD intensities of the (111), (200), (020) and (220) peaks indicate the preferential development of the $a$-$b$-plane orientation in the sintered bodies.

Figure 5 shows changes in Lotgering factor ($L_f$) and relative density (RD) with MF applied during slip casting for samples sintered at 900°C [(A) and (C)] and 1000°C [(B) and (D)]. Closed triangles indicate $L_f$ values of BIT samples without Nd$^{3+}$.

Forming $^{14-16}$ The increasing XRD intensities of the (111), (200), (020) and (220) peaks indicate the preferential development of the $a$-$b$-plane orientation in the sintered bodies.

Figure 5 shows changes in Lotgering factor ($L_f$) and relative density (RD) with the strength of MF for 25Nd-BIT samples sintered at 900°C [(A)] and 1000°C [(B) and (D)]. Closed triangles indicate $L_f$ values of BIT samples without Nd$^{3+}$.

Fig. 5. Changes in $L_f$ (solid lines) and relative density (broken lines) with MF applied during slip casting for samples sintered at 900°C [(A) and (C)] and 1000°C [(B) and (D)]. Closed triangles indicate $L_f$ values of BIT samples without Nd$^{3+}$.

Fig. 6. SEM images of selected BNIT samples fabricated at different MFs and sintering temperatures; (A) 0 T and 900°C, (B) 4 T and 900°C, (C) 0 T and 1000°C and (D) 4 T and 1000°C.

Fig. 6. SEM images of selected samples fabricated at different MFs and sintering temperatures; (A) 0 T and 900°C, (B) 4 T and 900°C, (C) 0 T and 1000°C and (D) 4 T and 1000°C.

Fig. 7. Temperature dependences of $\varepsilon_r$ for 25Nd-BIT samples obtained by forming at (A) 0 T, (B) 2 T, (C) 4 T and (D) 12 T and sintering at 1000°C (Dotted lines are for $\tan \delta$).

Fig. 7. Temperature dependences of $\varepsilon_r$ for 25Nd-BIT samples obtained by forming at (A) 0 T, (B) 2 T, (C) 4 T and (D) 12 T and sintering at 1000°C (Dotted lines are for $\tan \delta$).
forming at various MFs and sintering at 1000°C for 4 h. Each sample has a broadened $\xi$, peak at around 250°C, which could be correlated with structural transformation. A substantial increase in $\xi$ is observed when the applied MF is raised from 0 to 2 T, indicating the enhanced ion displacement along the $a$-axis in grain-oriented BNIT ceramics.

4. Discussion

The magnetically stable axis of the diamagnetic solid particles is oriented preferentially towards the direction of the MF applied. The magnetic susceptibility of diamagnetic BLSFs satisfies $\Delta \chi = \chi_{ab} - \chi_{c} > 0$, where $\chi_{c}$ and $\chi_{ab}$ are the magnetic susceptibilities along the $c$-axis and the $a$-$b$-plane in the crystal, respectively. Therefore, the magnetic stability of the axes perpendicular to the $c$-axis would be larger than that of the $c$-axis. Previous studies on the fabrication of [hk0]-oriented BIT ceramics using a very strong MF revealed that the magnetically stable axis of the diamagnetic BIT crystal could be one perpendicular to the $c$-axis. For the paramagnetic BNIT that was modified by cation substitution with Nd$^{3+}$, the (Bi$_2$O$_2$)$_2$ layers in the crystal structure changed its magnetic property from diamagnetic to paramagnetic. This change results from the incorporation of magnetic Nd$^{3+}$ ions into the lattice sites of non-magnetic Bi$^{3+}$ ions. The relationship given by $\Delta \chi = \chi_{a-b} - \chi_{c} > 0$ for the magnetic susceptibilities of BIT is basically ascribed to the strong anisotropy in the crystal structure of BIT.

If the anisotropic nature of the BIT structure is not changed by the substitution with Nd$^{3+}$ cations which are mostly incorporated in the (Bi$_2$O$_2$)$_2$ layers, then the relationship of $\Delta \chi = \chi_{a-b} - \chi_{c} > 0$ holds in the paramagnetic BNIT. Thus, it is considered that little change in the magnetic anisotropy between diamagnetic BIT and paramagnetic BNIT resulted in the similar behavior of the preferential particle alignment under MF conditions for both materials.

The particle size of a powder to be formed under MF conditions has been found to affect the degree of particle (grain) orientation in a sample. Doshita et al. examined the effect of powder properties on the degree of crystal orientation of BIT ceramics fabricated by a high-MF method. The degree of the orientation exhibited little dependence on the crystallinity of the powder. However, $L_{fi}$ of [hk0]-oriented BIT ceramics increased with increasing $D_{50}$ (the median diameter) from 0.5 to 1.2 µm. The particle size dependence of the crystal orientation was explained by Langevin’s theory on magnetic alignment. Therefore, a low $L_{fi}$ value obtained in this study for the 0Nd-BIT sample formed at 12 T, which is considerably different from the results already reported, could be attributed to the very small BIT particles in the slurry. The 25Nd-BIT samples, on the contrary, show substantially increased $L_{fi}$ values as can be seen in Fig. 5. The improved alignment of very fine BNIT particles during MF-assisted forming is ascribed to the magnetic property change from diamagnetic (BNI) to paramagnetic (BNIT), because no appreciable differences in the average size and shape of the synthesized powders were detected between 0Nd- and 25Nd-BIT samples.

$L_{fi}$ values are larger for BNIT ceramics sintered at 1000°C than those sintered at 900°C. This difference was considered to be due to the effect of grain growth during sintering. $L_{fi}$ and RD changes with sintering time at 1000°C and the corresponding microstructure evolution during sintering are shown in Figs. 8 and 9, respectively. The RD values become very high in 10 min, indicating that most of the densification has been completed during heating period to 1000°C. The $L_{fi}$ change, however, indicates a gradual increase with sintering time after 10 min. Figure 9 clearly shows that increasing sintering times caused simultaneous increases in (1) the average grain size, (2) aspect ratio of elongated plate-like grains and (3) fractional content of largely elongated grains. These results reveal that the degree of grain orientation is closely related to the microstructure development during sintering. A similar close relation was reported in template grain growth (TGG) study of BIT ceramics, in which only 5 vol% template particles were used and highly [00] oriented BIT ceramics were obtained due to the preferential growth of the template particles. In the present study, remarkable growth of anisotropic plate-like grains occurred at later stage of the sintering. Therefore, the preferential growth of anisotropic grains with the $a$-$b$-plane perpendicular to the direction of MF largely contributed to the fabrication of grain-oriented BNIT ceramics by
sintering at 1000°C.

5. Conclusion

A Nd-modified Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ (BNIT) powder, in which 25% of the Bi$^{3+}$ cations were substituted with an equal amount of Nd$^{3+}$ cations, was prepared by coprecipitation in an alkaline solution and successive calcination at 600°C to examine the degree of the grain orientation of BNIT ceramics fabricated by applying magnetic-field-assisted (MF-assisted) forming at lower MFs. After slip casting in a mold under various MF conditions, dried compacts were sintered at 900 and 1000°C for different times. The cation substitution with Nd$^{3+}$ changed their magnetic properties from diamagnetic (BIT) to paramagnetic (BNIT). However, it caused no change in their magnetic behaviors that the $c$-axis of the BIT-based structure could be aligned normally to the applied MF, thus producing $[hk0]$-oriented BNIT ceramics.

For BNIT ceramics sintered at 1000°C, Lotgering factor ($L_f$) was found to increase with increasing MF according to the parabolic relationship given by $L_f^2 \propto K(MF)$, where $K$ is a constant, i.e., $L_f = 0.35, 0.50$ and $0.59$ at 2, 4 and 8 T, respectively. SEM observation showed that the preferentially enhanced growth of largely anisotropic BNIT grains occurred at later stage of the sintering, leading to the increased grain orientation. Thus, grain-oriented BNIT ceramics with the $a$-$b$-plane perpendicular to the direction of MF were successfully fabricated by MF-assisted forming at lower MFs.

References

19) ICCD card number 72-1019.