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

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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 Bi^{3+}-site were substituted with Nd^{3+}, 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 Nd^{3+} allowed very fine BNIT particles in a slurry to be magnetically aligned at lower field strengths. For BNIT ceramics sintered at 1000°C, the degree of grain orientation increased with increasing MF according to the parabolic relationship. Additionally, the grain orientation was enhanced by the preferential growth of anisotropic BNIT grains occurring at later stage of the sintering.

Key-words : $Bi_4Ti_3O_{12}$, Cation substitution with Nd^{3+}, Magnetic-field-assisted forming, Grain orientation, Preferential grain growth

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1. Introduction

Ferroelectric Aurivillius compounds (BLSFs) have a unique crystal structure which is composed of bismuth oxide based layers, $(Bi_2O_2)^{2+}$, interleaved with pseudo-perovskite-type layers, $(A_{m-1}B_mO_{3m+1})^{2-}$ where A and B are large and small cations, respectively, and m is an integer showing the number of the octahedral BO_6 unit constituting the pseudo-perovskite-type layers.[1)] Most of the compounds have been promising candidate materials for high temperature piezoelectric applications, because they are Pb-free and have high Curie temperatures.[1),2)] Among the Aurivillius family, $Bi_4Ti_3O_{12}$ (BIT) with m = 3 has been extensively studied due to its large spontaneous polarization character.[1)] It has a substantially large spontaneous polarization (P_s) of ~50 μC/cm² along the *a*-axis of a single crystal, whereas a value along the *c*-axis is much suppressed to 4 μC/cm², showing a large anisotropy in its ferroelectric property.[3)–5)]

For electroceramics with very strong anisotropic properties, the production of grain-oriented ceramics is required to take advantage its excellent property. Several procedures have been attempted for the production of grain-oriented BIT ceramics. The grain orientation was successfully achieved by applying mechanically uniaxial compaction to green bodies containing more or less plate-like BIT powder, i.e. by hot-forging,[6)] cold-forging[7)] and hot-pressing[8),9)] processes. In addition, the usage of shear stress in a slurry consisting of a mixture of plate-like and fine BIT particles, such as tape casting, was found to be effective for aligning morphologically anisotropic BIT particles.[10)–12)] In the grain-oriented BIT ceramics thus fabricated, however, enlarged surfaces of plate-like particles were aligned perpendicular to the direction of the uniaxial compaction or parallel to the shear stress, producing BIT ceramics with a laminated texture of well-developed *c*-plane. This indicated that they had a low P_s or P_r (remnant polarization) along the laminated direction.

Recently, a new method has been employed to improve the grain orientation of the BIT ceramics.[13)] It is called a magnetic-field-assisted (MF-assisted) forming process and has more advantageous feature in controlling the orientation of a desired crystal plane than other procedures mentioned above. Under a magnetic field (MF) condition, the *c*-plane of the diamagnetic BIT structure is oriented parallel to the applied field.[14)] This fact reveals that the (*h*00)- or (*hk*0)-plane (*a*-*b*-plane) can easily align normal to the MF, producing BIT ceramics with a large polarization directed to the MF (sample thickness). After the publication of the study on the application of MF-assisted forming,[13)] the process has been intensively used to fabricate grain-oriented BIT and other BLSF ceramics.[14)–18)] In most of the studies, a very high MF larger than 10 T has been applied in the forming process, because such a large MF, which can be generated by a superconducting magnet, is necessarily required to cause effectively the particle alignment in a green body consisting of diamagnetic particles. If the particle orientation with the *a*-*b*-plane stacked in a direction of the sample thickness can be readily achieved by applying a substantially low MF for BIT ceramics, the extensive application of a cost-effective and energy-saving MF-assisted forming process using a conventional electrically-inductive magnet will be expected. In this study, therefore, grain-oriented BIT ceramics were fabricated by using a Nd^{3+}-modified BIT powder and slip cast forming under various MF conditions from 2 to 12 T in order to examine the degree of the grain orientation caused by lower MFs.

2. Experimental procedure

Fixed amounts of chemically pure Bi_2O_3 and Nd_2O_3 (both from Kojundo Co., Japan) were dissolved in an aqueous HNO_3 solution, to which a given amount of Ti-tetraisopropoxide was

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added. A transparent HNO_3 solution containing Bi^{3+}, Nd^{3+}, and Ti^{4+} 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 polycarboxylate (ALON A-6114, Toagosei 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 alumina 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, $L_f = (P - P_0)/(1 - P_0)$ where $P = \Sigma I$ (selected peak)$/\Sigma I$ (hkl) 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 $2\theta = 10$ 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 (ε_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 ($S_w = 18.7\,m^2/g$) 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.

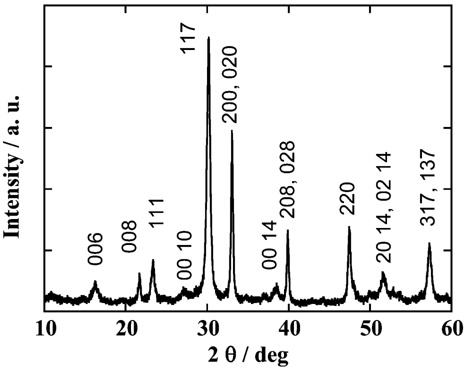

Fig. 1. XRD pattern of 25Nd-BIT powder calcined at 600°C.

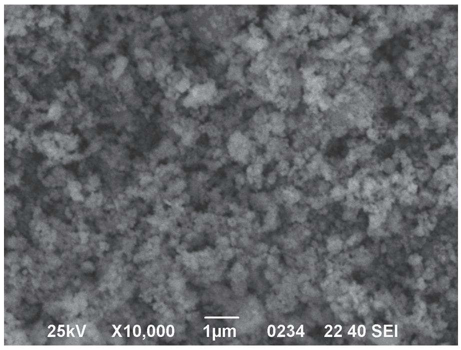

Fig. 2. Powder morphology of calcined 25Nd-BIT.

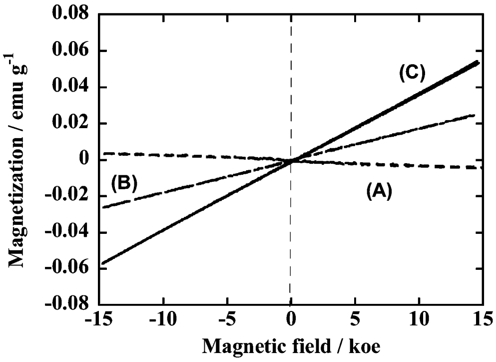

Fig. 3. Magnetic property change of calcined BIT powders substituted with Nd^{3+}; (A) 0%, (B) 12.5% and (C) 25.0%.

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.[19] 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

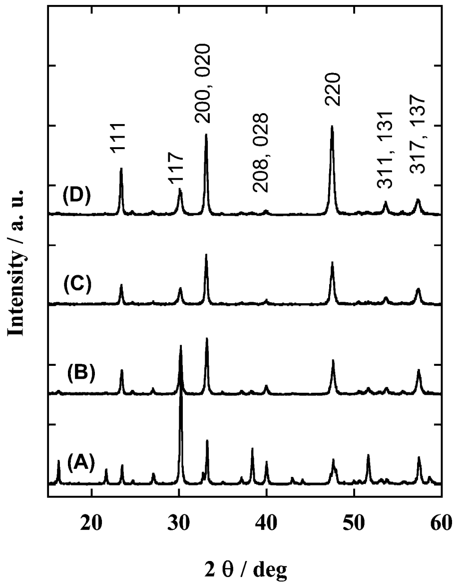

Fig. 4. XRD patterns of BNIT samples formed at different MFs of (A) 0 T, (B) 2 T, (C) 4 T and (D) 8 T and sintered at 1000°C.

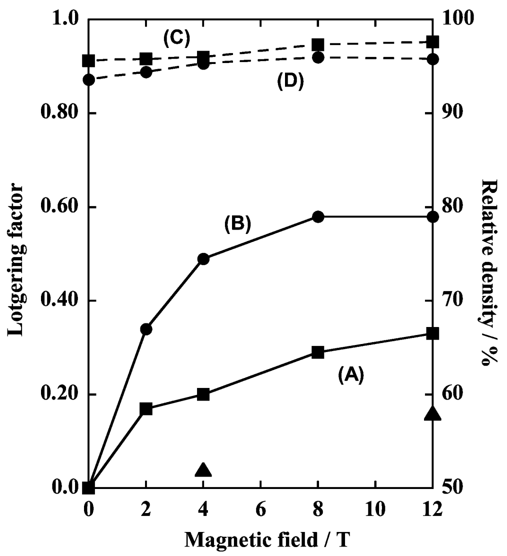

Fig. 5. Changes in L_f (solid lines) and relative density (broken lines) with MF applied during slip casting for samples sintered at 900° [(A) and (C)] and 1000°C [(B) and (D)]. Closed triangles indicate L_f values of BIT samples without Nd^{3+}.

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 and 1000°C. RDs of ceramic bodies sintered at both temperatures exceed 94% of the theoretical value and tend to increase very slightly with increasing MF. Contrast to the little change in the RD, the degree of grain orientation varied significantly depending on applied MF and sintering conditions. The 0Nd-BIT samples show substantially small L_f values, even formed at 12 T. Appreciable increases in L_f, on the contrary, are clearly seen for the 25Nd-BIT samples sintered at both temperatures. Especially, samples sintered at 1000°C show a considerably high value ($L_f = 0.35$) even at 2 T, and was followed by a parabolic increase given by $L_f^2 \propto K(MF)$, where K is a constant, with a maximum value ($L_f = 0.59$) at 8 T. For those sintered at 900°C, L_f values were smaller for all MF.

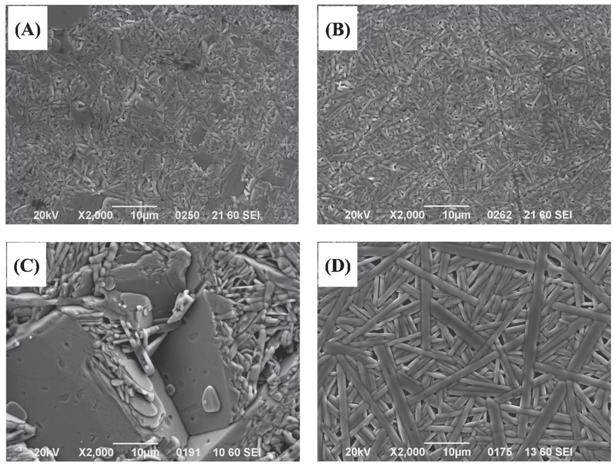

Fig. 6. SEM images of selected BNIT samples fabricated at different MFs and sintering temperatures; (A) 0 T and 900°C, (B) 4 T and 900°C, (C) 0 T and 1000°C and (D) 4 T and 1000°C.

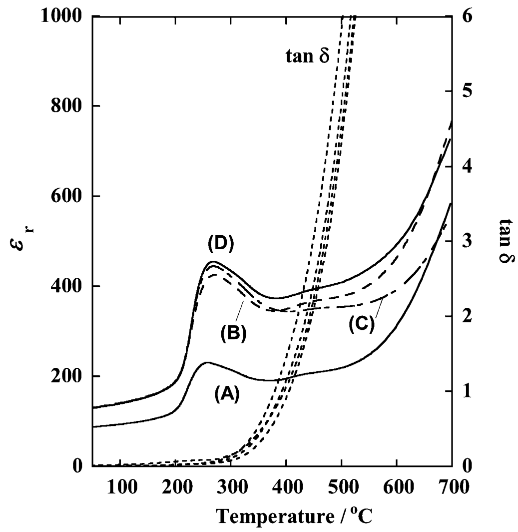

Fig. 7. Temperature dependences of ε_r for 25Nd-BIT samples obtained by forming at (A) 0 T, (B) 2 T, (C) 4 T and (D) 12 T and sintering at 1000°C (Dotted lines are for $\tan\delta$).

SEM images of selected samples are presented in **Fig. 6**. The samples sintered at 900°C are composed of considerably small grains with low aspect ratios. Remarkable grain growth occurred after sintering at 1000°C. A significant effect of MF applied during slip casting on the microstructure can be also seen in the SEM images of the samples obtained at 1000°C [Figs. 6(C) and 6(D)]. Plate-like grains having very large areas are attached each other with their surfaces stacked in a face-to-face manner and distributed randomly in a sample formed without MF. For grain-oriented samples [Fig. 6(D)], many edge planes with very large aspect ratios, which correspond to the *a*-*b*-plane of the BIT crystal, are arranged with their surfaces perpendicular to the direction of the applied MF.

Figure 7 shows the temperature dependences of dielectric permittivity (ε_r) measured for 25Nd-BIT ceramics fabricated by forming at various MFs and sintering at 1000°C for 4 h. Each sample has a broadened ε_r peak at around 250°C, which could be correlated with structural transformation. A substantial increase in ε_r 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.[14] The magnetic susceptibility of diamagnetic BLSFs satisfies $\Delta\chi = \chi_{a\text{-}b} - \chi_c > 0$, where χ_c and $\chi_{a\text{-}b}$ 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.[14] Previous studies on the fabrication of [*hk*0]-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+} in this study, the XRD analysis in which diffraction intensities of the (111), (200, 020) and (220) peaks increased with increasing strength of MF (Fig. 4) showed that the *c*-axis of the modified BNIT structure could be aligned normally to the applied MF. As is described in the section 3.1 of this paper, it becomes clear that the cation substitution with Nd^{3+} for the Bi^{3+}-sites in the BIT structure changes its magnetic property from diamagnetic to paramagnetic. This change results from only the incorporation of magnetic Nd^{3+} ions into the lattice sites of non-magnetic Bi^{3+} ions. The relationship given by $\Delta\chi = \chi_{a\text{-}b} - \chi_c > 0$ 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 $(Bi_2O_2)^{2+}$ layers, then the relationship of $\Delta\chi = \chi_{a\text{-}b} - \chi_c > 0$ 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. Doshida et al. examined the effect of powder properties on the degree of crystal orientation of BIT ceramics fabricated by a high-MF method.[14] The degree of the orientation exhibited little dependence on the crystallinity of the powder. However, L_f of [*hk*0]-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_f value obtained in this study for the 0Nd-BIT sample formed at 12 T, which is considerably different from the results already reported,[13)–16)] could be attributed to the very small BIT particles in the slurry. The 25Nd-BIT samples, on the contrary, show substantially increased L_f 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_f 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_f 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_f 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*l*]-oriented BIT ceramics were obtained due to the preferential growth of the template particles.[20] 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

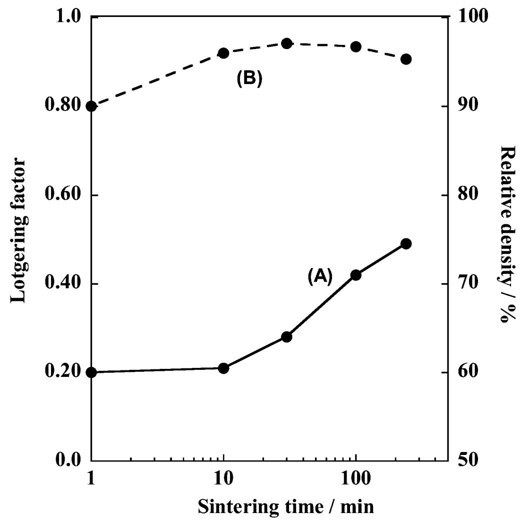

Fig. 8. Changes in (A) L_f and (B) relative density with sintering time at 1000°C for 25Nd-BIT samples formed at 4 T.

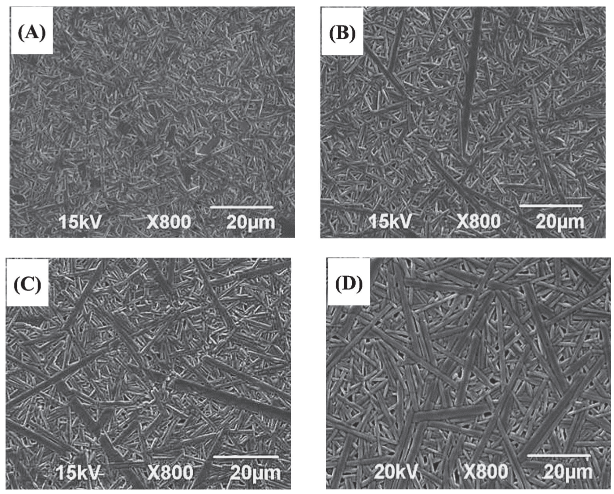

Fig. 9. Microstructure evolution showing grain growth of 25Nd-BIT samples formed at 4 T and sintered at 1000°C for (A) 10 min, (B) 30 min, (C) 100 min and (D) 240 min.

sintering at 1000°C.

5. Conclusion

A Nd-modified $Bi_{4-x}Nd_xTi_3O_{12}$ (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 [*hk*0]-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.

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