

Piezoelectric properties of textured $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{2.97}\text{V}_{0.03}\text{O}_{12}$ ceramics fabricated by reactive templated grain growth method

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Abstract We have fabricated $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{2.97}\text{V}_{0.03}\text{O}_{12}$ (BLTV) ceramics by reactive templated grain growth method using a $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ template and investigated the electromechanical coupling coefficient (k) and temperature coefficient of a resonant frequency as a function of temperature. The highly preferentially $[00l]$ oriented BLTV ceramics were obtained and the grain-orientation factor (Lotgering factor) was 83%. The electromechanical coupling coefficient of the longitudinal vibration mode (k_{33}) and the temperature coefficient of resonant frequency of textured BLTV ceramics were enhanced compared to those of nontextured BLTV ceramics.

Keywords Lead-free · Reactive templated grain growth · Piezoelectricity · Bismuth titanate

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1 Introduction

In recent years, bismuth layer-structured ferroelectrics (BLSF) have been intensively investigated as novel ferroelectric materials to replace conventional Pb-based ferroelectrics [1] (e.g., PbTiO_3 and $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$) because of their excellent piezoelectric and ferroelectric properties. BLSF are characterized by their low dielectric constant, high Curie temperature, and large anisotropy in the electromechanical coupling [2–5]. Therefore, the BLSF ceramics are seen as superior candidates for lead-free piezoelectric materials with high Curie temperature and anisotropic characteristics.

One of the BLSF compounds, Lanthanum and vanadium co-substituted bismuth titanate ($\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{2.97}\text{V}_{0.03}\text{O}_{12}$, BLTV) ceramics and thin films are reported with high ferroelectric performance such as high dielectric strength, relatively large remanent polarization (P_r), low coercive field (E_c), and low leakage current. Therefore BLTV compounds are candidates for lead-free piezoelectric materials [6–9].

In this paper, in order to improve the lead-free piezoelectric ceramics, we study the effect of grain orientation in the lead-free $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{2.97}\text{V}_{0.03}\text{O}_{12}$ ceramics. We have prepared two kinds of samples. One type of ceramics was fabricated by a conventional solid state reaction method. Whereas other type textured ceramics, was fabricated by the reactive templated grain growth (RTGG sample) using plate-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ particles. We have investigated their ferroelectric and piezoelectric properties.

2 Experimental procedure

The textured BLTV ceramics were fabricated by the reactive templated grain growth technique [15–18]. The oxide powders of Bi_2O_3 , La_2O_3 , TiO_2 and V_2O_5 of above 99.9% purity were used as raw materials. BLTV powder was obtained by ball-milling and solid-state reaction. The raw powders were ball-milled in methyl alcohol with zirconia balls for 10 h. The milled solids were dried and then heated in a covered alumina crucible at 750 °C for 2 h. The plate-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT) particles were used as templates. BiT platelets were prepared from Bi_2O_3 and TiO_2 using molten-salt synthesis. Bi_2O_3 and TiO_2 were mixed in the molar ratio of 2:3 and ball-milled as described above. After drying, the ball-milled oxides were mixed with an equimolar mixture of NaCl and KCl (weight ratio of oxides to salt=1:1) and heated in a covered alumina crucible at 1050 °C for 2 h in air atmosphere. After heat treatment, NaCl and KCl were removed by washing with deionized water. Repeated washing by settling and decantation was used to isolate the plate-like BiT particles. During the washing, an AgNO_3 solution was used as a qualitative test for Cl^- ion in the wash liquid. Washing was continued until the addition of nitrate solution to the wash liquid produced no visible turbidity. BiT platelets with an average diameter of 5–10 μm and a thickness of 0.5 μm were obtained. The BiT platelets were mixed with calcined BLTV powder. The amount of BiT platelets was 15 wt.% to BLTV powder. Additional amounts of La_2O_3 , TiO_2 , and V_2O_5 to the stoichiometry were included in the mixing batch to react with the BiT.

The powders were mixed with a solvent (60 vol.% methyl ethyl ketone–40 vol.% ethyl alcohol) in a ball mill for 20 h, and then polyvinyl butyral (binder) and di-*n*-butyl phthalate (plasticizer) were added and mixed for 1 h. The slurry was tape-cast to form a sheet with a thickness of ~0.15 mm on SiO_2 coated polyethylene film by using a doctor-blade technique. The green sheet was cut and laminated at 45°C under 30 MPa for 5 min to form green compacts with thickness of ~5 mm. The green compacts were heated at 400 °C for 56 h in air atmosphere to remove organic ingredients and then sintered at 1100 °C for 2 h in air atmosphere. The sintered compacts were cut into parallel [//] and perpendicular [\perp], respectively, to the tape-casting direction for measuring the physical properties of the textured BLTV ceramics. Nontextured BLTV ceramics were also prepared by the conventional process (CP). The BLTV powder was obtained by ball-milling and solid-state reaction at 750 °C for 2 h and uniaxially pressed at 50 MPa and sintered at 1100°C for 2 h. The crystalline phases and the degree of orientation were determined using X-ray diffraction (XRD) analysis on the major surface (the same as the sheet surface) of the sintered specimen. The

microstructure of the sintered ceramics was observed using scanning electron microscopy (SEM) on thermal etched surface parallel and perpendicular to the major face. For electrical measurements, the specimen was cut into small pieces, and silver electrodes were deposited on both sides of the specimens using a dc sputtering. The ferroelectric P – E hysteresis loops were measured by a Sawyer–Tower circuit. For piezoelectric measurement, the specimen was poled in silicon oil at 200 °C with a dc field of 4 kV/mm for 1 h. Piezoelectric properties were measured by resonance–antiresonance method using an impedance analyzer HP 4194A. The temperature coefficient of resonant frequencies was measured in the temperature range between 20 and 100 °C.

3 Results and discussion

Figure 1 shows two types of specimens in textured BLTV ceramics. Textured BLTV ceramics were sliced parallel and perpendicular to the casting direction for measurements of anisotropic physical properties. From now on, the specimens sliced parallel and perpendicular to the casting direction are abbreviated as RTGG[//] and RTGG[\perp], respectively. In addition, the nontextured BLTV specimens, prepared by conventional process, are abbreviated to CP.

Figure 2 shows the microstructures of BiT platelets, RTGG[//], RTGG[\perp], and CP specimens. The CP ceramics were composed of randomly oriented plate-like grains as shown in Fig. 2(d). However, the RTGG specimen (fabricated by RTGG process using BiT templates) was textured as shown in Fig. 2(b) and (c). During the tape-casting of BLTV slurry, which included BiT platelets, plate-like BiT particles were aligned parallel to the tape-casting direction. During the sintering process, BiT platelets combined with La_2O_3 , TiO_2 , and V_2O_5 to form plate-like BLTV. The plate face was parallel to the casting direction, and the thickness was slightly larger than original BiT.

Figure 3 shows the XRD patterns of BLTV powder, RTGG[\perp] and RTGG[//] specimens. The diffraction peaks of all specimens consisted of only a single phase of layered perovskite structure without a secondary phase. In a CP

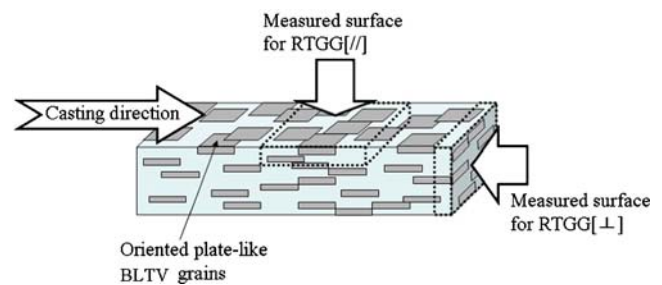


Fig. 1 Configuration of specimen and surfaces for measurement

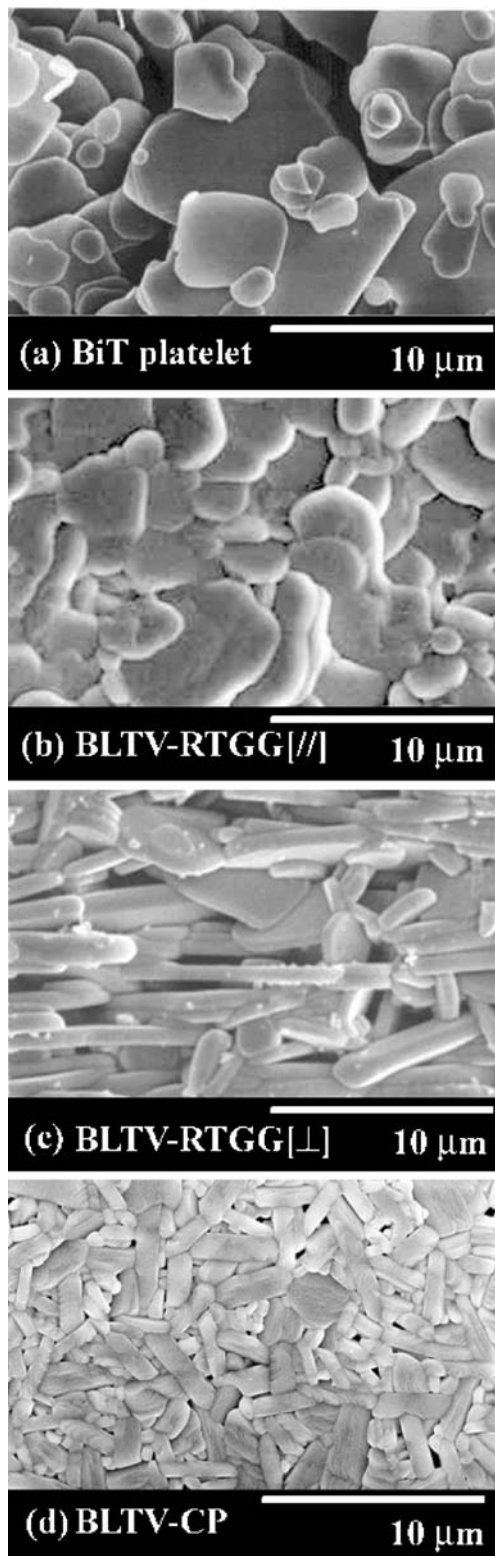


Fig. 2 SEM images of (a) BiT platelets, (b) BLTV-RTGG[//], (c) BLTV-RTGG[⊥], and (d) BLTV-CP specimens

specimen (nontextured ceramic), $\{117\}$ is the main peak. In contrast, the intensity of $\{00l\}$ peaks of RTGG[//] specimen was increased relatively to the CP specimen. The change of intensity represents an increase in the crystallographic $\langle 00l \rangle$ orientation of the polycrystalline BLTV ceramics. In case of BNKT[⊥] specimen, the intensity of $\{200\}$, $\{020\}$ and $\{220\}$ peaks was enhanced relatively than that of $\{00l\}$ peaks. Therefore, this indicate that the RTGG[//] specimens were preferentially oriented to the c -axis and the direction of c -axis was almost parallel to the stacking direction. The RTGG[⊥] was preferentially oriented to $a(b)$ -axis which was perpendicular to the stacking direction. The degree of orientation, F , was calculated using the following equation (Lotgering method) [10].

$$F = \frac{P - P_0}{1 - P_0}, \quad P = \frac{\sum I\{00l\}}{\sum I\{hkl\}}, \quad P_0 = \frac{\sum I_0\{00l\}}{\sum I_0\{hkl\}} \quad (1)$$

Where I and I_0 are the peak heights of the RTGG[//] and CP specimens, respectively, and $\{00l\}$ and $\{hkl\}$ are the Miller indices. The diffraction peaks between 20° and 60° were used to calculate P and P_0 . The textured BLTV ceramics prepared by RTGG method have 83% of $\langle 00l \rangle$ preferred orientation toward parallel to the stacking direction.

Figure 4 shows the P - E hysteresis loops of CP, RTGG[⊥], and RTGG[//] specimens in BLTV ceramics. The remanent polarization (P_r) and coercive field of the CP specimen were $11 \mu\text{C}/\text{cm}^2$ and $46 \text{ kV}/\text{cm}$, respectively. The P_r of RTGG[⊥] and RTGG[//] specimens were 26.2 and $0.5 \mu\text{C}/\text{cm}^2$, respectively. Bismuth layer structured compounds consist of bismuth oxide layers and pseudo-perovskite blocks [2]. The direction of the spontaneous polarization on the bismuth layer structured compounds was almost parallel to the a -axis. In the investigation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ single crystals, it was determined that the

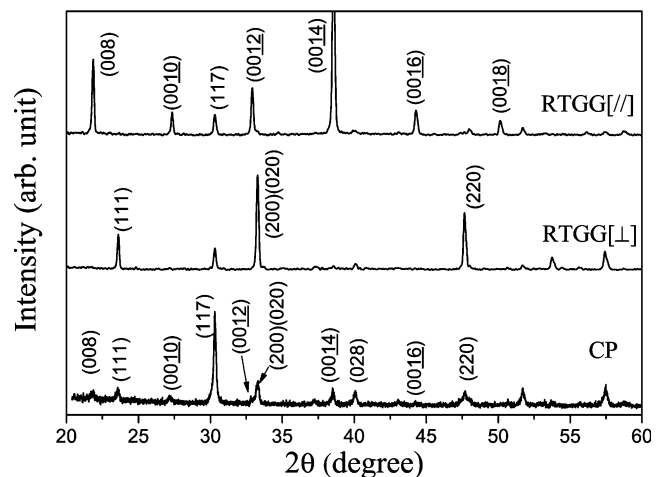


Fig. 3 XRD patterns of BLTV powder, BLTV-RTGG[⊥], and BLTV-RTGG[//] specimens

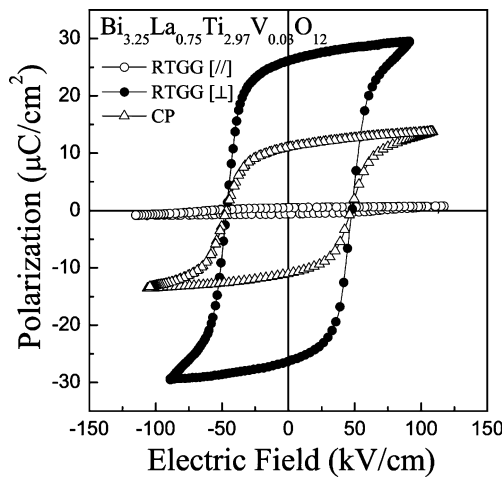


Fig. 4 P–E hysteresis loops for CP, RTGG[⊥], and RTGG[//] specimens

direction of the spontaneous polarization changed easily by applying an electric field parallel to the *a*(*b*)-axis, and hardly by changed applying an electric field parallel to the *c*-axis [11–14]. Therefore, the value of P_r for RTGG[⊥], which was preferentially oriented to *a*(*b*)-axis, was higher than those of other specimens.

The electromechanical coupling coefficient *k* and the temperature dependence of resonant frequency of the CP and RTGG specimens were measured. Figure 5 shows the poling direction and configuration of a longitudinal vibration mode (33 mode) and thickness shear 15 vibration modes for BLTV-RTGG ceramics. According to the result of *P*–*E* hysteresis loops measurement, the BLTV-RTGG ceramics were poled with applying an electric field perpendicular to the stacking direction which determined three-axis. Then the specimen was cut into 33 and 15 vibration mode sample as shown in Fig. 5.

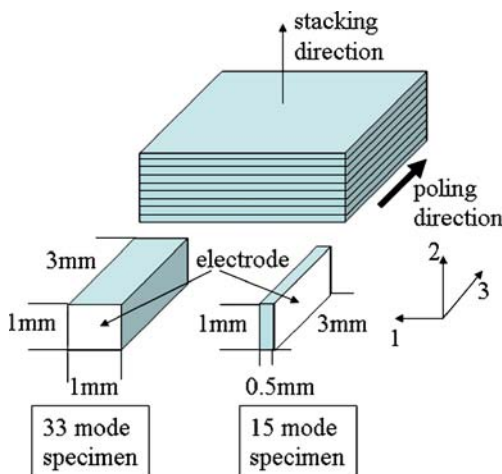


Fig. 5 The poling direction and configuration of longitudinal vibration mode (33 mode) and thickness shear 15 vibration modes for grain oriented BLTV ceramics

Table 1 Electromechanical coupling coefficients and temperature coefficient of resonance frequency of CP and RTGG specimen.

| Sample | | <i>k</i> (%) | <i>d</i> ₃₃ (pC/N) | TCF (ppm/ °C) |
|--------|---------|--------------|-------------------------------|---------------|
| CP | 33 mode | 22 | 17 | –85 |
| RTGG | 33 mode | 28 | 33 | –69 |
| | 15 mode | 29 | | –50 |

Table 1 shows the electromechanical coupling coefficients and the temperature coefficient of resonance frequency (TCF) of each mode in the CP and RTGG specimens. The electromechanical coupling coefficient of the longitudinal vibration mode (*k*₃₃) of BLTV-RTGG specimen is 28%, which is larger than that of the CP specimen. It seems that an increase in the coupling coefficient *k* is due to the arrangement of the *c*-axis to one direction and the faces including the polarization axis directed parallel to the poling direction. Figure 6 shows the temperature dependence of the resonant frequency on the 33 vibration mode of the CP specimen, and the 33 and 15 vibration modes of the RTGG specimen. The TCF was calculated from the slope of the temperature dependence of the resonant frequency for the each specimen. The TCF of BLTV-RTGG specimen was –69 ppm/ °C, which was about 20% lower than that of the CP specimen due to the difference of crystal symmetry between <00> textured and nontextured BLTV ceramics. The crystal symmetry of <00> textured BLSF ceramics is lower than that of randomly oriented ceramics because the symmetry of the textured ceramics is denoted as mm2 (*C*_{2v}), while that of randomly oriented ceramics is denoted as ∞mm (*C*_∞) [19].

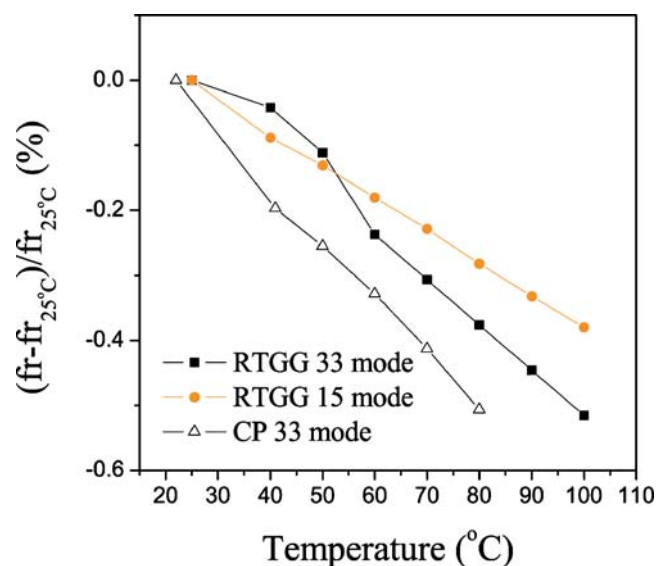


Fig. 6 Temperature coefficient of resonance frequency for BLTV-RTGG and CP specimen

Therefore, the grain orientation for bismuth layer-structured compounds improves the piezoelectric properties. The k_{15} and TCF of the thickness shear 15 vibration mode of the RTGG specimen were 29% and -50 ppm/°C, respectively. The resonance frequency of thickness shear 15 vibration mode was more stable under temperature variation than that of 33 vibration mode. Several piezoelectric devices, such as filter or oscillator, are required to have excellent temperature stability. In such case, using 15 vibration mode is better than 33 vibration mode.

4 Conclusions

To develop lead-free piezoelectric ceramics, we have fabricated BLTV ceramics by RTGG method using $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ template and investigated electromechanical coupling coefficient (k) and TCF as a function of temperature. The textured BLTV ceramics prepared by RTGG method have 83% of $\langle 00l \rangle$ preferred orientation toward parallel to the stacking direction. The k_{33} of textured BLTV specimen was 28%, which was larger than that of the nontextured specimen, found. The TCF of textured BLTV specimen was -69 ppm/°C, which was about 20% lower than that of the nontextured specimen, observed. Therefore, the grain orientation for bismuth layer structured compounds improves the piezoelectric properties.

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