

## Fabrication and High-Power Piezoelectric Characteristics of Textured $(\text{Sr}_{0.7}\text{Ca}_{0.3})_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ Ceramics

粒子配向型 $(\text{Sr}_{0.7}\text{Ca}_{0.3})_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ 系セラミックスの作製と

ハイパワー圧電特性

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### 1. INTRODUCTION

Recently, many high-power piezoelectric ceramic devices, such as ultrasonic motors and piezoelectric actuators, have been developed. Hard  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  [PZT] ceramics or  $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  [PMN-PZT] ceramics are usually used in high-power applications. However, PZT ceramics contain a large amount of  $\text{PbO}$ , therefore, lead-free piezoelectric materials to replace PZT are recently required from the viewpoint of environmental protection. One of the characteristics required for the ultrasonic transducer is vibration velocity. This is known to be proportional to the product of piezoelectric strain constant  $d_{33}$  and mechanical quality factor  $Q_m$ . Bismuth layer-structured ferroelectrics (BLSFs) have a high mechanical quality factor,  $Q_m$ . Therefore they are seemed to improve vibration velocity of lead-free piezoelectric materials<sup>[1]</sup>.  $(\text{Sr}_{0.7}\text{Ca}_{0.3})_2\text{Bi}_4\text{Ti}_5\text{O}_{18} + 0.2 \text{ wt}\% \text{MnCO}_3$  (SCBT) ceramics are one of possible candidate materials for high-power applications because they have high mechanical quality factor ( $Q_m = 5100$ ) and vibration velocity ( $v_{0-p} < 2.5 \text{ m/s}$ )<sup>[2]</sup>. However, SCBT ceramics have a small piezoelectric strain constant, ( $d_{33} = 20 \text{ pC/N}$ ). To solve this problem, we tried to make textured SCBT ceramics by using a hot-forging (HF) method. In this study, high-power piezoelectric characteristics of textured SCBT ceramics were investigated. Then, grain orientation effects on their piezoelectric properties in SCBT system are also studied, comparing them with ordinarily fired (OF) non-oriented ones.

### 2. EXPERIMENTAL PROCEDURE

Ceramic samples were prepared by a conventional ceramic fabrication technique. The starting raw materials were  $\text{Bi}_2\text{O}_3$  of 99.99% of purity,  $\text{TiO}_2$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$  and  $\text{MnCO}_3$  of 99.9% of purity. Calcination temperature was  $850^\circ\text{C}$  for 2 h and then sintering temperature was  $1200$ - $1240^\circ\text{C}$  for 2 h in air. Grain-oriented samples were prepared by the hot-forging (HF) method. The grain orientation factor,  $F$ , was calculated using the Lotgering method. Electrodes were made with fired-on Ag paste for electrical measurements such

as dielectric, ferroelectric and piezoelectric properties. Applied field,  $E_p$ , temperature,  $T_p$ , and time,  $t_p$ , in the poling process were about  $4.5$ - $6 \text{ kV/mm}$ ,  $200^\circ\text{C}$  and 7 min, respectively. A longitudinal vibration of the (33) mode was measured using a rectangular specimen of  $2 \times 2 \times 5 \text{ mm}^3$ . Small amplitude piezoelectric properties were determined by a resonance and antiresonance method using a impedance analyzer (Agilent 4294A). A piezoelectric transducer was driving by a function generator (NF WF1943A) and a power amplifier (NF HAS4052). The vibration velocity  $v_{0-p}$  of the (33) mode was measured using a laser Doppler vibrometer (Ono Sokki LV1710) with an oscilloscope (Tektronix TDS3054B). The vibration velocity  $v_{0-p}$  of the short time driving was determined by a frequency sweep measurement around resonant frequency. On contrary, the long time driving was measured under the condition of constant voltage at resonant frequency.

### 3. RESULTS AND DISCUSSION

HF-SCBT ceramics sintered at  $1200^\circ\text{C}$  showed single phase BLSF structure ( $m=5$ ), and high relative density of approximately 96.5%. The degree of grain orientation,  $F$ , determined by the Lotgering method was over 95%. This means that the high density, high textured and single-phase SCBT can be prepared by using HF method. The resistivity of this sample at RT was  $3 \times 10^{13} \Omega \cdot \text{cm}$ .

Figure 1 shows the frequency dependences of impedance,  $|Z|$ , and phase,  $\theta$ , of HF-SCBT ceramic. In the case of OF-SCBT +  $\text{MnCO}_3$  0.2 wt% samples, mechanical quality factor,  $Q_m$ , and piezoelectric constant,  $d_{33}$ , were 5100 and 20.2 pC/N, respectively. On the other hand, the HF-SCBT showed relatively high  $Q_m$  and  $d_{33}$  values of 5500 and 33.7 pC/N, respectively. Piezoelectric properties of OF and HF-SCBT ceramics are summarized in Table I, showing that the the product of  $d_{33} \times Q_m$  of HF-SCBT is approximately twice as large as that of OF-SCBT. Figure 2 shows the applied field  $E_a$  dependences of vibration velocity  $v_{0-p}$  for OF and HF-SCBT ceramics measured under continuous driving. As the result, the vibration

velocity of HF-SCBT was larger than that of OF-SCBT. This is due to the enhancement of the  $d_{33} \times Q_m$  product. Figure 3 shows the vibration velocity  $v_{0-p}$  dependences of resonant frequency shift for OF and HF-SCBT ceramics measured under continuous driving. These frequency shifts are quite small as a function of vibration velocity and they are almost similar to each other. Figure 4 shows the electrical current,  $I$ , as a function of vibration velocity  $v_{0-p}$  under continuous driving for OF and HF-SCBT ceramics. The  $I$  of HF-SCBT was larger than that of OF-SCBT at the same vibration velocity. The force factor  $A$  is obtained from the amplitude of the current divided by the amplitude of the vibration velocity. Therefore, it shows the force factor  $A$  of HF-SCBT is larger than that of OF-SCBT ceramics.

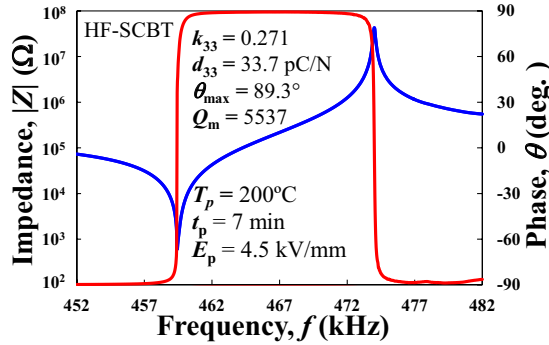


Fig. 1 Frequency dependence of impedance,  $Z$ , for HF-SCBT ceramic.

Table I Electrical and piezoelectric properties of small amplitude vibration for OF and HF-SCBT ceramics.

	$\epsilon_{33}^T/\epsilon_0$	$k_{33}$ [%]	$d_{33}$ [pC/N]	$Q_m$	$d_{33} \times Q_m$ [nC/N]	$Z_{min}$ [Ω]	$\theta_{max}$ [deg.]
OF-SCBT	202	16.4	20.2	5100	103	2330	87.2
HF-SCBT	241	27.1	33.7	5537	187	603	89.3

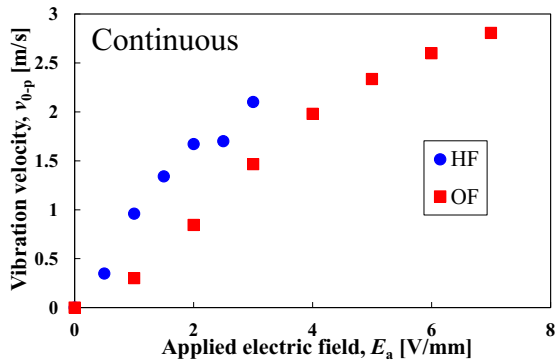


Fig. 2 Applied field  $E_a$  dependences of vibration velocity  $v_{0-p}$  for OF and HF-SCBT ceramics.

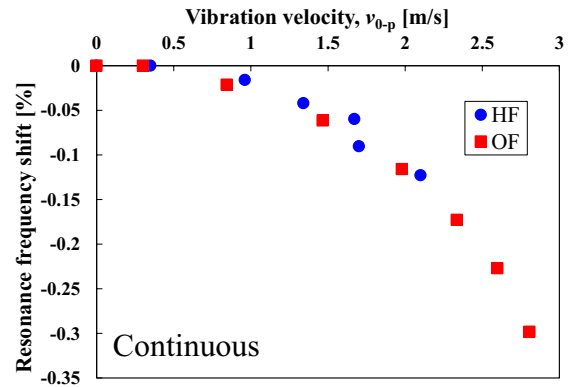


Fig. 3 Vibration velocity  $v_{0-p}$  dependences of resonant frequency shift for OF and HF-SCBT ceramics.

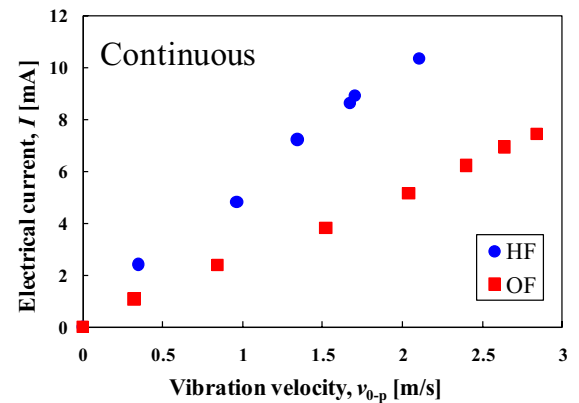


Fig. 4 Electrical current,  $I$ , as a function of vibration velocity  $v_{0-p}$  for OF and HF-SCBT ceramics.

## 4. CONCLUSIONS

High-power piezoelectric characteristics at continuous driving of the textured bismuth layer-structured ferroelectrics  $(\text{Sr}_{0.7}\text{Ca}_{0.3})_2\text{Bi}_4\text{Ti}_5\text{O}_{18} + 0.2 \text{ wt}\% \text{MnCO}_3$  (HF-SCBT) and non-oriented ones (OF-SCBT) were studied. The vibration velocity of HF-SCBT was larger than that of OF-SCBT. Also, the resonance frequency shifts of OF and HF-SCBT were less than 0.15% at  $v_{0-p}$  of 2.0 m/s. The force factor  $A$  of HF-SCBT was improved compared with that of OF-SCBT ceramics, which was caused by the enhancement of piezoelectric strain constant,  $d_{33}$ , by the grain orientation. Therefore, HF-SCBT is superior candidate for high-power applications such as ultrasonic transducer with less drive voltages and frequency stabilities.

## REFERENCES

- 1) H. Ogawa, S. Kawada, M. Kimura, K. Shiratsuyu, and Y. Sakabe: IEEE trans. on UFFC. **54** (2007) 2500.
- 2) H. Nagata, M. Seki, Y. Noumura, and T. Takenaka: Jpn. J. Appl. Phys. **50** (2011) 09ND05.