Piezoelectric properties in textured ceramics of bismuth layer-structured ferroelectrics

M. Kimura · H. Ogawa · T. Sawada · K. Shiratsuyu · N. Wada · A. Ando

Abstract Piezoelectric properties and their temperature stability were studied for the <001> textured ceramics of bismuth layer structured ferroelectrics $SrBi_2Nb_2O_9$ (SBN) type compound. The <001> textured ceramics of 10% Nd substituted SBN were obtained by the templated grain growth (TGG) method, and the orientation degree reached 96%. Electro-mechanical coupling coefficient of thickness shear vibration for the 96%-textured specimen was three times larger than that for the randomly oriented specimen. In addition, the resonance frequency increased with increasing temperature for the 96%-textured specimen, while it decreased for the randomly oriented specimen. Therefore, textured ceramics with various orientation degrees were prepared. The gradient of the temperature variation in the resonance frequency changed from negative to positive with increasing grain orientation, and an excellent temperature coefficient of resonance frequency (TCF) of −0.4 ppm/°C was obtained for the specimen with 76% orientation. Moreover, the specimens with the major faces formed at various angles to <001> oriented direction were fabricated from a 96%-textured ceramics. The gradient of temperature variation in resonance frequency changed from negative to positive with decreasing angle. the minimum value of TCF was −2.6 ppm/°C for the specimen with a 30° angle. Optimization of the orientation degree or the major face angle was effective to improve TCF for thickness shear vibration of SBN type ceramics.

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1 Introduction

Bismuth layer-structured ferroelectrics (BLSF) have large crystal anisotropy [1], and the piezoelectricity of the polycrystaline ceramics is generally smaller than that of widely used perovskite-type piezoelectric ceramics [2]. Therefore, textured ceramics of BLSF have been studied to improve their piezoelectric properties in the last few decades. Several methods were examined to obtain textured ceramics. Hot-forging, templated grain growth (TGG) method and reactive TGG method were proposed [3–5], and highly <001> textured ceramics were obtained for $Bi_4Ti_3O_{12}$, $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ and $CaBi_4Ti_4O_{15}$ [6–8]. It was reported that the electro-mechanical coupling coefficients and piezoelectric constants of highly textured BLSF ceramics were two or three times larger than those of randomly oriented ceramics.

Temperature stability of the piezoelectric properties is also important for practical usage. Especially, high accuracy of resonance frequency is necessary for piezoelectric filter or resonator applications. We have tried to improve the temperature stability of BLSF ceramics for these applications, and it was shown that a small temperature coefficient of resonance frequency (TCF) for the thickness shear vibration is obtained in <001> textured $CaBi_4Ti_4O_{15}$ ceramics [9]. The crystal symmetry of poled, <001> textured BLSF ceramics is lower than that of poled, randomly oriented ceramics. The symmetry of the poled, textured ceramics is denoted as mm2 (C_{2v}), while that of poled, randomly oriented ceramics is denoted as ∞mm

(C_∞). Therefore, 24 mode vibration separates from 15 mode vibration in the case of thickness shear vibration for the textured ceramics [10]. The TCF of the 15 mode vibration for textured ceramics was smaller than those of the 15 mode vibration for randomly oriented ceramics and the 24 mode vibration for textured ceramics, and electromechanical coupling coefficient of the 15 mode vibration for textured ceramics was larger than those of the 15 mode vibration for randomly oriented ceramics and the 24 mode vibration for textured ceramics [9].

On the other hand, the piezoelectric characteristics of $SrBi_2Nb_2O_9$ (SBN) were first reported by Subbarao in 1962 [11]. It is known that SBN has a low electro-mechanical coupling coefficient around 15% and a high mechanical quality factor around 2,000. It has been also reported that SBN has a relatively small TCF of about −20 ppm/°C, compared to other BLSF, and that the TCF further decreases with Ba or Nd substitution on the Sr site [12–16]. From these points, the SBN type compounds have been considered as candidate materials for fine tolerance filter or resonator applications.

However, few studies have ever been examined textured SBN type compound ceramics. In this study, textured SBN type ceramics were obtained by the TGG method, and the piezoelectric properties of the thickness shear vibration were evaluated. The dependence of orientation degree upon the piezoelectric properties and TCF were also studied. Moreover, specimens with the major faces formed at various angles to the oriented direction were fabricated from the textured ceramics, and their properties were determined.

2 Experimental procedure

2.1 Preparation of plate-like particles

The starting raw materials were high purity $SrCO_3$, Nd_2O_3, Bi_2O_3, Nb_2O_5 and $MnCO_3$ (99.9%). They were weighed with the composition represented by the following chemical formula,

$$Sr_{0.9}Nd_{0.1}Bi_2Nb_2O_9 + 0.2wt.\%MnCo_3.$$
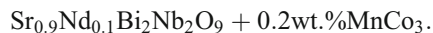
Nd was substituted on the Sr site to obtain template particles with large shape anisotropy, which were required for fabricating highly textured ceramics by the TGG method [17]. $MnCO_3$ was added as a sintering aid. The weighed powder was ball-milled with deionized water and calcined at 800 °C for 2 h. The template particles were prepared by a molten salt synthesis with KCl flux. The calcined powder was mixed with an equal weight of high purity KCl (99.5%) and heated in a high purity alumina crucible at the temperatures from 1,000 to 1,200 °C for

10 h. After heating, those mixtures were washed with deionized water to remove KCl flux. The dimension of plate-like template particles varied from approximately 3.0 to 7.5 μm in diameter, and the aspect ratio ranged from about 4 to 7.

2.2 Textured ceramics with various orientation degrees

The normally calcined powder was ball-milled again with deionized water, and average diameter of the milled powder was 0.8 μm. Then, the template particles and the calcined powders were mixed with the weight ratio of 1:4, respectively, and tape-casting slurries were prepared by adding 10 wt.% polyvinyl acetate based binder to these mixtures. The green tapes were prepared with a thickness of 60 μm by the doctor-blade technique. They were stacked and pressed into green bodies with a thickness of 5 mm under a pressure of 10 MPa. After that, the green bodies were heated at 500 °C for 2 h to remove the binder, and fired at 1,200 °C for 5 h in an oxygen atmosphere. The textured ceramics with various orientation degrees were fabricated using template particles with a wide range of the average diameter. Randomly oriented ceramics were also prepared using the same process without the template particles. The sintered ceramics were poled perpendicular to the tape stacking direction under the electric field of 10 kV/mm for 30 min in silicone oil at 200 °C.

2.3 Textured specimens with various major face angles

The 15 and 24 mode vibration resonator specimens were prepared by cutting the textured ceramics into plates parallel and perpendicular to the stacking direction, respectively. The 15 mode vibration should be excited in plates with the major faces parallel to both the tape stacking direction, which corresponded to the <001> oriented direction, and the poling direction. On the other hand, the 24 mode vibration should be excited in plates with major faces perpendicular to the stacking direction and parallel to the poling direction. Specimens with the major faces formed at angles of 15, 30 and 45° to the stacking direction were also fabricated. Figure 1 shows the relationship between the stacking direction of the textured ceramics and the major face of the specimens.

2.4 Measurements

The density of the sintered ceramics was measured by the Archimedes method. Microstructure was observed by scanning electron microscopy (SEM), and crystalline structure was evaluated by the X-Ray diffraction (XRD) technique. The orientation degree was determined from the XRD profiles using the Lotgering method [18]. Piezoelec-
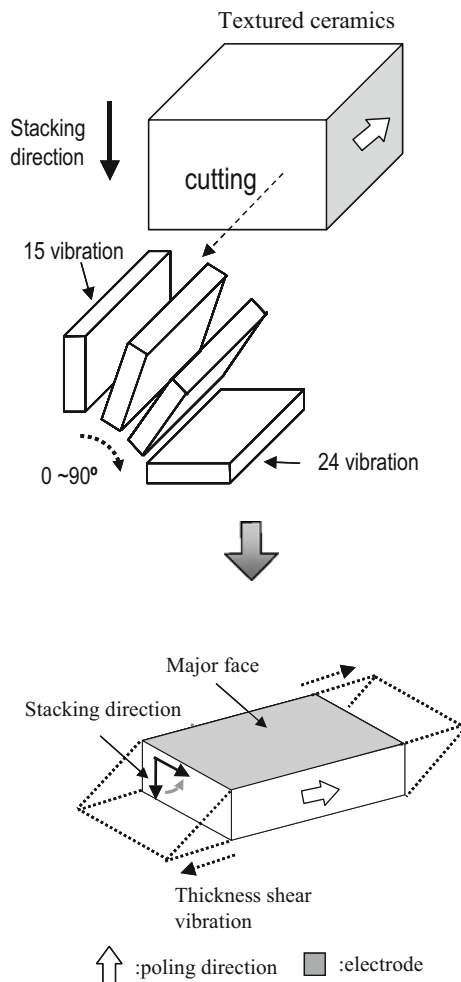
Fig. 1 Schematic figure of the resonator specimens for the texture ceramics with various major face angles. The textured ceramics were cut into plates with the major faces formed at angles of 0° (15 mode vibration), 15°, 30°, 45° and 90° (24 mode vibration) to the stacking direction, and five types of resonator specimens for thickness shear vibration were obtained from these plates

tric properties were measured by the standard resonance method (IEEE) using an impedance/gain phase analyzer. TCF was calculated by the following formula,

$$\text{TCF} = (f_{\max} - f_{\min})/(f_{r25°C} \cdot 100),$$

where $f_{r\ \max}$ and $f_{r\ \min}$ are the maximum and minimum values of resonance frequency within a temperature range of −20 to 80 °C, respectively, and $f_{r25\ °C}$ is the resonance frequency at 25 °C. TCF is defined as a positive number in the case where the resonance frequency increases with increasing temperature, and as a negative number in the case where the resonance frequency decreases with increasing temperature.

Silver electrodes were made on the major faces of the specimens by sputtering method. All specimens had dimensions of 3.0 mm (length)×0.5 mm (width)×0.3 mm (thickness).

3 Results and discussion

3.1 Textured ceramics with a high orientation degree

Textured ceramics with an orientation degree of 96% were obtained using template particles with an average diameter of 7.5 μm. The relative density of these ceramics achieved 98%.

Figure 2(a) and (b) show XRD profiles for the polished face perpendicular to the stacking direction of the textured ceramics and the ground powder of randomly oriented ceramics, respectively. The intensity of each <001> peak for the textured ceramics was much stronger than that for the powder, on the contrary, the intensity of other reflections was weak. Therefore, it was recognized that the ceramics were highly <001> oriented parallel to the stacking direction.

Figure 3(a) and (b) show SEM micrographs of the surfaces perpendicular and parallel to the stacking direction for the textured ceramics, respectively. It indicated that most of the plate-like grains aligned perpendicular to the stacking direction.

Dielectric and piezoelectric properties were summarized for the textured 15 and randomly oriented 15 mode specimens in Table 1. The Curie temperature and relative dielectric permittivity $\varepsilon_{11}^{T}/\varepsilon_0$ of the textured specimen were almost the same as those of the randomly oriented specimen. The electro-mechanical coupling coefficient k_{15} and piezoelectric constant d_{15} of the textured 15 mode vibration specimen were three times and twice larger than those of the randomly oriented 15 mode vibration specimen, respectively. Mechanical quality factor Q_m of the textured 15 mode vibration specimen was also larger than that of the randomly oriented specimen.
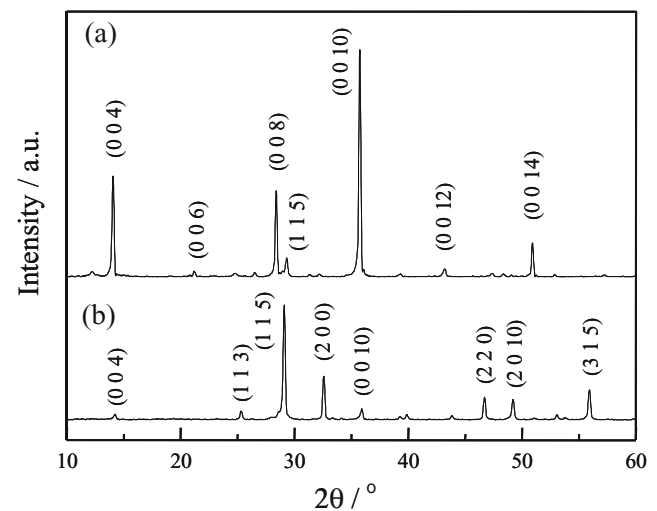

Fig. 2 XRD profiles for (a) the surface perpendicular to the stacking direction of the 96%-textured ceramics and (b) the ground powder of randomly oriented ceramics
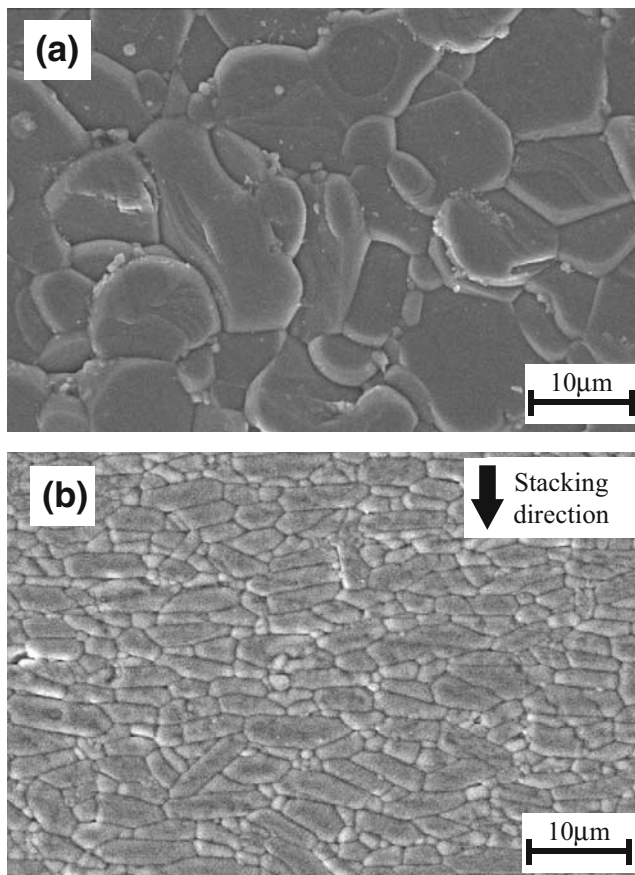
Fig. 3 SEM micrographs of the 96%-textured ceramics. (**a**) and (**b**) show the surfaces of perpendicular and parallel to the stacking direction, respectively

TCF of the textured specimen was also different from that of the randomly oriented specimen. The TCF of the 96%-textured ceramics was +20.9 ppm/°C, while that of the randomly oriented ceramics was −30.6 ppm/°C. The absolute value of TCF for the textured specimen was two thirds of that for the randomly oriented specimen. However, the temperature dependence of resonance frequency for the highly textured ceramics showed completely different behavior compared with the randomly oriented ceramics, although the temperature dependences of resonance frequency for the highly textured and randomly oriented CBT ceramics indicated similar behavior [9]. In this work, the resonance frequency decreased with increasing temperature for the randomly oriented specimen; on the contrary, the

Table 1 Piezoelectric properties of the textured ceramics.

	96%-textured	Randomly oriented
Curie temperature/°C	390	390
Dielectric permittivity $\varepsilon_{11}^{T}/\varepsilon_0$	160	165
Coupling coefficient k_{15}/%	24.8	8.2
Piezoelectric constant d_{15}/pC/N	32	14
Mechanical quality factor Q_m	2,950	2,400

resonance frequency increased with increasing temperature for the textured specimens. This result suggested that the TCF of textured SBN ceramics can be remarkably improved using grain orientation control.

3.2 Textured specimens with various orientation degrees

Textured ceramics with the orientation degree from 54 to 82% were fabricated using template particles of the dimension from 3.1 to 7.5 μm in diameter. The relative density of all specimens was over 97%. Figure 4 shows the temperature dependence of resonance frequency of the 15 mode vibration for the textured and the randomly oriented specimens. The resonance frequency varied linearly with increasing temperature for all specimens. However, their gradients were drastically different. These changed from negative to positive with increasing grain orientation, and the absolute value of TCF became smallest for the 76%-textured specimen.

Figure 5 shows the dependence of TCF and electromechanical coupling coefficient k_{15} on the orientation. The TCF increased linearly with increasing the orientation degree, and the minimum value of TCF was −0.4 ppm/°C at the specimen with orientation degree of 76%. The k_{15} also increased linearly with increasing the orientation degree, and the k_{15} was 20.2% at the specimen with orientation degree of 76%.

3.3 Textured specimens with various major face angles

Specimens with the major faces formed at angles of 0, 15, 30, 45 and 90° to the stacking direction were fabricated for the 96%-textured ceramics, and the dependence of TCF and electro-mechanical coupling coefficient on the angle between the major face and the <001> oriented direction was
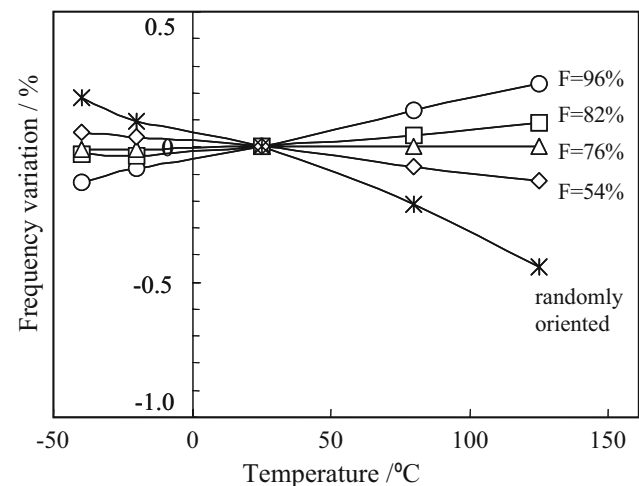

Fig. 4 Temperature dependence of resonance frequency for textured 15 vibration specimens with orientation degrees (F) from 54 to 96%, and the randomly oriented 15 vibration specimen
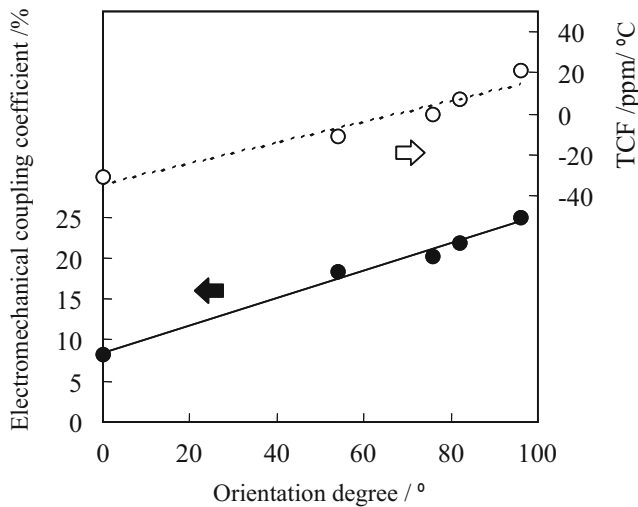
Fig. 5 Dependence of TCF and electro-mechanical coupling coefficient on the orientation. The orientation degree of randomly oriented specimen was assumed to be 0°

Fig. 7 Dependence of TCF and electro-mechanical coupling coefficient on the angle between the major face and the <001> oriented direction

studied for the thickness shear vibration. The specimen with angles of 0 and 90° corresponded to the 15 and the 24 mode vibration, respectively. Figure 6 shows the temperature dependence of the resonance frequency for the specimens with angles from 0 to 90°. The resonance frequency varied linearly with increasing temperature for all specimens, and their gradients changed from negative to positive with decreasing angle.

Figure 7 shows the dependence of TCF and electro-mechanical coupling coefficient on the angle between the major face and the <001> oriented direction, respectively. The TCF decreased linearly with increasing angle, and the minimum value of TCF was −2.6 ppm/°C for the specimen with an angle of 30°. The electro-mechanical coupling coefficient also decreased linearly with increasing angle, and the electro-mechanical coupling coefficient was 19.5%
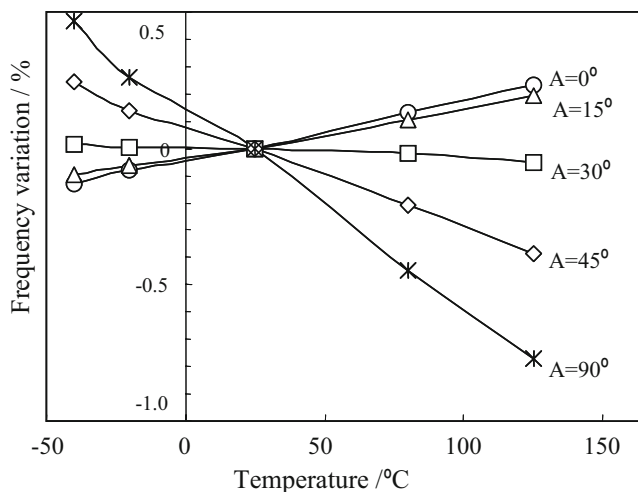
at the specimen with the angle of 30°. It is probable that intermediate characteristics between the 15 and 24 mode vibration were observed for the specimens with the angle of 15, 30 and 45°.

The dependence of the angle is similar to that of TCF and electro-mechanical coupling coefficient on orientation, and the piezoelectric properties of the specimen with the angle of 45°, which is midway between 15 and 24 vibration modes, was approximately the same as the randomly oriented samples. These results suggest that intermediate characteristics between the 15 and 24 mode vibration could be obtained in the case of changing the orientation degree also.

4 Conclusions

Highly <001> textured ceramics were obtained for 10% Nd substituted $SrBi_2Nb_2O_9$ by the TGG method, and the orientation degree measured using the Lotgering method was 96%. The electro-mechanical coupling coefficient of the thickness shear vibration for the 96%-textured specimen was 24.8%, which was three times larger than that for the randomly oriented specimen. The temperature coefficient of the resonance frequency (TCF) for the textured specimen was +20.9 ppm/°C. The resonance frequency increased with increasing temperature for the textured specimen, while the resonance frequency decreased with increasing temperature for the randomly oriented specimen.

Textured ceramics with the orientation degrees from 54 to 96% were prepared using various diameter template particles to control TCF. The gradient of temperature variation in the resonance frequency changed from negative to positive with increasing grain orientation, and an excellent TCF of −0.4 ppm/°C was obtained for the specimen with

Fig. 6 Temperature dependence of resonance frequency for 96%-textured specimens. The samples had their major faces formed at angles of (A) of 0, 15, 30, 45 and 90° to the stacking direction
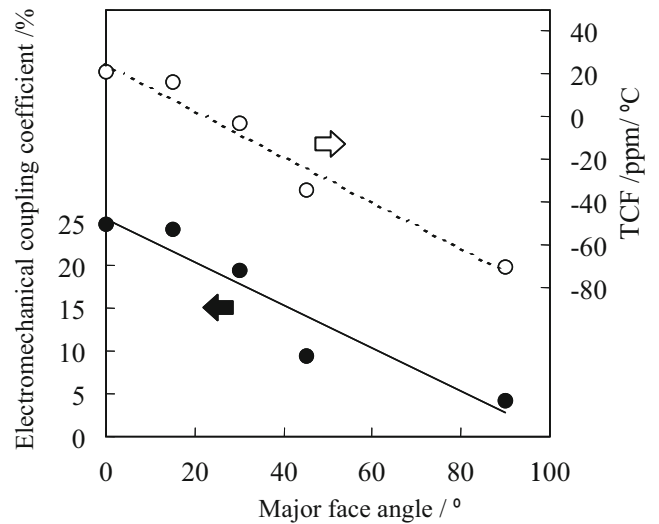
orientation degree of 76%. The electro-mechanical coupling coefficient of the specimen was 20.2%.

The specimens with the major faces formed at various angles to the <001> oriented direction were prepared for the 96%-textured ceramics. The gradient of temperature variation in resonance frequency changed from negative to positive with decreasing angle. The minimum value of TCF was −2.6 ppm/°C for the specimen with the angle of 30°.

Optimization of the orientation degree or the angle between the major face and <001> oriented direction was shown to be valuable to obtain excellent TCF for thickness shear vibration of SBN type ceramics. Textured SBN ceramics should be strong candidates for the fine tolerance resonator applications.

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