Grain Orientation and Electrical Properties of Hot-Pressed Bismuth Titanate Ceramics

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ホットプレスしたチタン酸ビスマスセラミックスの 粒子配向と電氣的性質

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Introduction

Hot-pressing is one of the important preparation methods of grain-oriented ferroelectric and piezoelectric ceramics¹⁾. The effects of processing parameters on the grain orientation, however, are not fully understood. This paper deals with the effect of the particle shape of starting powders on the grain orientation. Lumpy and plate-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders with controlled particle morphology were prepared by solid state method and molten salt synthesis²⁾, respectively. The degree of orientation was estimated by X-ray diffraction and dielectric constant. Piezoelectric property was measured also.

Experiments

The preparation method of starting powders are described elsewhere^{2),3)}. Briefly, stoichiometric mixtures of Bi_2O_3 and TiO_2 were heated with mixed sulfates (S) or chlorides (C) or without salt (N). $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders so obtained will be called by the abbreviated form of the salts used and preparation temperature (Table 1). Figure 1 shows the scanning electron microscope (SEM) photographs of the obtained $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders. The particle size and aspect ratio (plate

diameter/thickness) of the plate-like particles increased with increasing preparation temperature. The aspect ratio of powder C was larger than that of powder S, as compared at the same preparation temperature.

The powders were pressed uniaxially into pellets 15 mm in diameter and 20 mm in height under a pressure of 1000 kg/cm². The green compact was placed in an alumina die with ZrO_2 compaction powder and heated up to 800°C in vacuum and then to 1050°C in oxygen at the heating rate of 300°C/h. After the temperature reached 1050°C, the pressure of 200 kg/cm² was applied. After 5 h at 1050°C under pressure, the pressure was removed and the sample was cooled in the furnace. Ordinarily sintered pellet was also prepared under the same conditions without applied pressure. The sintered materials were cut into thin wafers in two directions as

Table 1. Preparation conditions of starting powders.

Sample	Flux	Temp. (°C)	Time (h)
N800		800	2
S800	Sulfates	800	6
S1050	Sulfates	1050	1
C800	Chlorides	800	6
C1050	Chlorides	1050	1

Fig. 1. Scanning electron microscope photographs of the starting powders.

Fig. 2. Preparation of wafers.

shown in Fig. 2. The cutting directions are represented based on the directional relation between the applied pressure and electric field.

The microstructural characteristics were determined on the wafer surfaces; the degree of orientation by X-ray diffraction analysis³⁾ and SEM observation on thermally etched surfaces. Gold electrodes were sputtered on the major surfaces and electrical properties such as temperature dependence of dielectric constant at 10 MHz, voltage-current characteristics at 150°C and electro-mechanical coupling factor k_t were determined by an impedance analyser.

Results and discussion

Figure 3 illustrates the X-ray diffraction profiles of the parallel wafers of hot-pressed and ordinarily fired S 1050 and N 800 powders with their measured faces perpendicular to the pressing direction. The intensity of (001) diffraction line increased by hot-pressing. Table 2 shows the degree of orientation. The degree of orientation of the ordinarily fired N 800 was 0 but that of plate-like powders was between 0.15 and 0.32,

Fig. 3. X-ray diffraction patterns of hot-pressed (HP) and ordinarily fired (OF) N 800 and S 1050. Circle indicates that the line belongs to (001).

Table 2. Density and degree of orientation of hot-pressed (HP) and ordinarily fired (OF) wafers.

Powder	Density (%)		Degree of Orientation		$\epsilon_{\perp}/\epsilon_{\parallel}$ HP
	HP	OF	X-ray HP	OF	
N800	99.9	94.4	0.87	0.00	4.1
S800	99.9	94.1	0.82	0.15	3.3
S1050	100.0	94.8	0.76	0.20	2.9
C800	99.9	89.8	0.77	0.22	3.3
C1050	99.9	88.9	0.82	0.32	3.6

indicating that the orientation was achieved to some extent in the green compacts of the plate-like powders. The hot-pressed wafer of N 800, on the other

Fig. 4. Scanning electron microscope photographs of hot-pressed (HP) and ordinarily fired (OF) N 800 and S 1050 (the faces are parallel to the pressing direction).

hand, had the largest degree of orientation. Figure 4 shows the SEM photographs of hot-pressed and ordinarily fired S 1050 and N 800 powders. As compared with Fig. 1, grain growth was evident and hot-pressing had no effect on the grain size. One of the microstructural characteristics of the ordinarily fired wafers was the large pores between the grains. No pores were observed in the hot-pressed specimens (densities are shown in Table 2). The plate-like grains have grown perpendicular to the hot-pressing direction.

Figure 5 illustrates the temperature dependence of dielectric constant of hot-pressed and ordinarily fired S 1050. Dielectric constant of the hot-pressed sample was highly anisotropic, especially near Curie temperature. The ratio of dielectric constants $\epsilon_{\perp}/\epsilon_{\parallel}$ at Curie temperature could be used as a measure of grain orientation and agreed well with that obtained by X-ray diffraction analysis (Table 2).

The fact that the hot-pressed N 800 had the largest degree of orientation might be explained as follows. The rate of grain growth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is larger along a axis than along c axis (crystal structure is tetragonal at 1050°C). In ordinarily fired N 800 the grains grow into plate-like shape (Fig. 4), but their orientation is

Fig. 5. Temperature dependence of dielectric constant of hot-pressed (HP) and ordinarily fired (OF) S 1050.

random, because every particle has a possibility of growth. In hot-pressed N 800, on the other hand, the uniaxial pressure would influence the rate of grain growth along the crystallographic axes. Thus, the particles having c axis parallel to the pressing direction have a larger possibility of growth and grow at the expense of other particles oriented in other directions, resulting in highly oriented plate-like grains. In the green compacts of plate-like powders, the particles were aligned to some extent, as judged

Fig. 6. Current-voltage characteristics of hot-pressed N 800 and S 1050 (V_b : Breakdown voltage).

from the degree of orientation in the ordinarily fired samples. The difference in growth rates between partially oriented particles would be smaller than that between randomly oriented particles, resulting in the growth of slightly misoriented grains and smaller degree of orientation. The degree of orientation of the ordinarily fired plate-like powders indicates that the larger degree of particle alignment in the green compact results in the larger grain orientation in the hot-pressed wafers except for S 800. In S 800 the degree of particle alignment is small and the sintering behavior would be close to a randomly packed compact.

Figure 6 illustrates the voltage-current characteristics of the hot-pressed S 1050 and N 800. In both specimens the parallel wafers had a larger electrical

Table 3. Electro-mechanical coupling factor of hot-pressed (HP) and ordinarily fired (OF) N 800 and S 1050.

Sample	Coupling Factor k_t		OF
	⊥	//	
N800	0.23	0.07	0.17
S1050	0.28	0.09	0.15

resistivity and breakdown voltage than those of perpendicular wafers. The wafers of N 800 had a larger resistivity than those of S 1050. Probably the residual sulfates used in the powder preparation reduced the resistivity.

The electro-mechanical coupling factor k_t was measured after poling at 30 and 15 kV/cm at 150°C for parallel and perpendicular wafers, respectively. The frequency-impedance characteristics of the wafers were measured and k_t was calculated from the frequencies of the maximum and minimum peaks. Table 3 shows k_t values of hot-pressed and ordinarily fired S 1050 and N 800. Anisotropy in k_t was obvious in the hot-pressed samples. A larger anisotropy could be expected from the spontaneous polarization (50×10^{-2} and 4×10^{-2} C/m² along a and c axes at room temperature⁴⁾). The smaller poling voltage due to the smaller breakdown voltage in the perpendicular wafers would be responsible for the smaller anisotropy than expected.

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