Improvement of Sintering Performances and Dielectric Properties of Oriented TiO₂ Ceramics Using Sintering Additives

Koichi Shigeno^{1, 2*} and Hirotaka Fujimori²

¹ National Institute of Technology, Ube College, 2-14-1 Tokiwadai, Ube City, Yamaguchi, JAPAN.

² Graduate School of Science and Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube City, Yamaguchi, JAPAN.

* Fax: +81-836-35-5294 and e-mail: shigeno@ube-k.ac.jp

We successfully examined effects of pulverization and an addition of sintering aids on the orientation degree, sintering performances, and dielectric properties of sintered compacts of needle-like TiO₂ particles. In the case of additive-free samples, an improvement in sintering performances was achieved by pulverization. However, the orientation degrees of these samples were decreased and calcination at high temperatures (≥ 1200 °C) was indispensable for obtaining an adequate relative density. On the other hand, by the addition of CuO-TiO₂-Nb₂O₅-Ag₂O type additives, the samples could be well sintered as much as 380 °C below their original sintering temperature with retaining the high orientation degrees. Moreover, high insulation resistances were achieved for samples with additives compared to that of additive-free samples and its relationship with the microstructures was discussed. Thus, this study provides an experimental investigation on improvements of sinterabilities and insulation properties of orientated TiO₂ ceramics by the use of sintering additives.

Key words: ceramic, TiO₂, orientation, sintering additive, dielectric property

1. INTRODUCTION

Ceramics produced by sintering process are generally polycrystalline in nature, and their properties depend on the average of those in each crystal direction. If ceramics can be oriented in a specific direction, it would be possible to obtain polycrystalline bulk ceramics with characteristics close to that of single crystals [1]. Therefore, oriented ceramics have been actively studied recently for improving properties such as piezoelectric, thermoelectric and paraelectric properties [2-6]. Methods to obtain oriented ceramics include extrusion, hot forge, templated grain growth (TGG), reactive templated grain growth (RTGG), and application of a magnetic field. However, one of the briefest ways is oriented consolidation of anisometric particles (OCAP) method using tape casting [2-6]. Oriented ceramics by OCAP method can be obtained by the following steps (Fig.1). Anisometric particles, such as plate-like or needle-like particles, are made into slurry that is formed into green sheets by tape casting, followed by stacking and sintering of the sheets. However, it has been said to be difficult to obtain densely packed sintered compacts using raw particles with anisometric shapes. Then, this has been adversely affected on the reliability of electronic ceramics [7-8].

The present study focuses on modification of ceramics by pulverization treatment and sintering additives. We specifically examined effects of pulverization time and the addition of sintering aids on the sintering performance, orientation degree and dielectric properties (relative permittivity, temperature coefficient of capacitance (TCC), and insulation resistance) using needle-like titanium oxide (TiO₂) particles, with paraelectricity oriented in the longitudinal direction.

Fig.1 Schematic diagram of OCAP method to produce oriented ceramics.

2. EXPERIMENTAL PROCEDURE

Experiments were carried out in accordance with the flow chart shown in Fig.2. For additive-free samples, needle-like TiO₂ particles (FTL-300, Ishihara Sangyo Co., Ltd.), which are elongated along the c-axis, were pulverized in a ball mill for 0, 6, 24, and 72 h and dried. For preparing samples with sintering additives, 95 mass% of the TiO₂ particles were mixed with 5 mass% of CuO-TiO₂-Nb₂O₅-Ag₂O type oxides, which were found to be effective in sintering of the alumina at low temperatures according to our previous studies [9-10]. The mixture was pulverized for 6 h. Subsequently, oriented ceramics were fabricated using the above-mentioned OCAP method. The resulting powders were made into slurry using an organic solvent, binder and a plasticizer, followed by forming 25 µm thick green sheets by tape casting, using the doctor blade method. Then, 18 sheets were stacked,

cut into required dimensions and debindered at 500 °C to form green compacts. Finally, the compacts were fired at temperatures of 850-1350 °C for 2 h in air atmosphere.

Fig.2 Experimental flow chart for obtaining oriented TiO₂ ceramics.

Fig.3 Schematic diagram of evaluation of the sample.

Bulk density and microstructure of the resulting sintered compacts were examined using a scanning electron microscope (SEM). Dielectric properties were measured, such as the relative permittivity and temperature coefficient of capacitance (TCC) in the stacking direction (as shown in Fig.3) at 1 MHz and insulation resistance at an applied voltage of 200 V (DC).

X-ray diffraction (XRD) analysis using CuK α radiation was carried out for evaluating the orientation degree. Lotgering F value ((F (hk0) in this study) was calculated by the Lotgering's method [11] using the following equations.

$$F(hk0) = \frac{P - P_0}{1 - P_0} \quad (1)$$

$$P = \frac{\sum I(hk0)}{\sum I(hkl)} \quad (2)$$

$$P_0 = \frac{\sum I_0(hk0)}{\sum I_0(hkl)} \quad (3)$$

where I and I_0 are intensities of diffraction lines of textured and randomly oriented samples, respectively. $hk0$ and hkl are the diffraction indices. The green compacts were also examined using XRD.

3. RESULTS AND DISCUSSION

Fig.4 shows SEM micrographs of the surface of TiO₂ green compacts with pulverization times of 0, 6, 24, and 72 h after burning out of the binder at 500 °C. Aspect ratios of the particles are found to decrease with an increase in the pulverization time.

Fig.4 SEM micrographs of the surface of TiO₂ green compacts with pulverization times of (a) 0 h, (b) 6 h, (c) 24 h, and (d) 72 h after burning out of the binder at 500 °C.

Fig.5 shows the XRD results of the above-mentioned samples. For reference, XRD pattern of the sample with equiaxial particles is also shown (Fig.5e). In the case of samples with short pulverization times, only peaks corresponding to $hk0$ reflections are observed. For example, F ($hk0$) of the sample with 6 h pulverization time is found to be more than 90 %. No significant differences in the XRD can be observed between samples with or without additives (the data is not shown in this figure). Prolonged pulverization results in an increase in the intensity of the peaks except for those of $hk0$ reflections. F ($hk0$) for the sample pulverized for 72 h decreases in 42 %, approaching 8 % of F ($hk0$) in the sample consisting of equiaxial particles.

Fig.5 XRD patterns of needle-like TiO₂ green compacts pulverized for (a) 0 h, (b) 6 h, (c) 24 h, and (d) 72 h. An XRD pattern of equiaxial TiO₂ green compact pulverized for 0 h is given for reference in (e). Diffraction indices of rutile type TiO₂ are indicated in the figure.

Fig.6 shows the relationship between the sintering density and the firing temperature of the samples. For the additive-free sample pulverized for 6 h, sintering at 1300 °C is indispensable for obtaining a sufficient relative density of 95 % against a theoretical density of a pure rutile type TiO₂, 4.26 g/cm³. The sintering performance is

improved with an increase in the pulverization time. However, the sample pulverized for 72 h is needed to be fired at 1200 °C for obtaining an adequate relative density. On the other hand, the sample containing 5 mass% of the additives and pulverized for 6 h exhibits a relative density of over 95 % when treated at a firing temperature of 920 °C. Thus, by the addition of the sintering aids, a lower sintering temperature of about 380 °C than that of the additive-free sample was achieved for the same pulverization time. The melting point of the sintering additives was found to be about 865 °C using thermogravimetry/ differential thermal analysis (TG/DTA). This result suggests that the liquid phase sintering is promoted at the temperatures higher than 865 °C. Moreover, it is assumed that CuO-Nb₂O₅-Ag₂O type additives induce similar sintering-promoted effects to the CuO-TiO₂-Nb₂O₅-Ag₂O type additives. Significant changes in the degree of orientation could not be observed with firing for all samples as shown in Fig. 7, although the intensities of 200 diffraction peaks tend to increase by densification. This indicates that the additives improve the sintering performance of the oriented TiO₂ ceramics without changing the orientation degree.

Fig. 6 Relationship between the sintering density and the firing temperature. Numbers shown in this figure indicate pulverizing time.

Fig. 7 XRD patterns of needle-like TiO₂ with CuO-TiO₂-Nb₂O₅-Ag₂O additives fired at (a) 1000 °C, (b) 950 °C, (c) 900 °C, and (d) 850 °C. An XRD pattern of a green compact is given for reference in (e).

Fig. 8 shows SEM micrographs of the sintered surfaces. For the additive-free sample, necking of the powder could not be observed at 1000 °C. In the case of samples with

additives, necking of powder clearly occurs at 850 °C. The grain growth is observed without any visible voids in the case of samples treated at 1000 °C.

Fig. 8 SEM micrographs of sintered surfaces after firing at each temperature for 2 h (upper row: additive-free samples, lower row: samples with additives).

Fig. 9 shows the relative permittivity and TCC values measured at 1 MHz as a function of orientation degree ($F(hk0)$) of the samples with sintering densities more than 4.0 g/cm³. The relative permittivity and absolute values of TCC decrease with an increase in the orientation degree. Relative permittivities of 170 in the direction along the c-axis and 86 in the direction perpendicular to the c-axis for rutile type TiO₂ have been reported [12], which reasonably matches with our results. Moreover, no significant differences in the dielectric properties are observed for samples in the presence and absence of additives.

Fig. 9 Relative permittivity and TCC of the samples at 1 MHz as a function of orientation degree, $F(hk0)$.

Sintering additives significantly affect the insulation resistances as can be observed from Fig. 10, which shows the relationship between the insulation resistance and the firing temperature. Prolonged pulverization increases the insulation resistance value. Furthermore, an increase of more than several hundred times of the insulation resistance is observed in the case of samples with sintering aids in comparison to additive-free samples, even with a short pulverization time of 6 h.

Figs. 10a and 10b show the SEM micrographs of the

additive-free sample fired at 1300 °C and the samples with additives fired at 1000 °C, respectively. Figs.10c and 10d show the energy dispersive X-ray spectra (EDS) of Cu and Ti in the latter sample, respectively. For the additive-free sample, many voids can be observed. In the case of the sample with additives, grain growth of TiO_2 particles is observed and each TiO_2 grain is surrounded by additive components, especially CuO, as oxygen can be detected in the whole area. In addition, voids are rarely visible. Therefore, the existence of additive components at the grain boundaries might be one of the reasons for the high insulation resistance.

Fig.10 Relationship between the insulation resistance (applied voltage: DC 200 V) and the firing temperature. Numbers in the figure indicate the pulverization time.

For reference, other sintering additives have also been developed for TiO_2 [13], and it would be interesting to examine the effects of different types of sintering additives.

Fig.11 SEM surface micrographs and EDS maps of oriented TiO_2 ceramics. (a) additive-free sample fired at 1300 °C, (b) sample with additives fired at 1000 °C, (c) Cu and (d) Ti spectra of (b) by EDS.

4. CONCLUSIONS

In this study, we fabricated oriented dielectric ceramics using needle-like TiO_2 particles and examined the effects of pulverization and sintering additives.

Effects of pulverization can be summarized as follows: a decrease in aspect ratios of particles, a decrease in the orientation degree and a slight improvement in sintering

performance were observed with an increase in the pulverization. The orientation degree ($F(hk0)$) and a dielectric property were found to depend on each other. Effects of sintering additives could be summarized as follows: orientation degree values were not significantly changed by the presence or absence of additives. However, sintering performance was improved drastically by the addition of sintering aids. Lower sintering temperature of about 380 °C than that of the additive-free sample was achieved for the same pulverization time. An increase of more than several hundreds times was observed in the insulation resistance values for samples containing additives compared to the additive-free samples. The existence of additive components at the grain boundaries as observed from the EDS analysis is assumed to be one of the reasons for this increase.

From the above results, the sintering additives used in this study are found to be effective in improving the sintering performance and the insulation resistance of oriented TiO_2 ceramics without significantly changing the orientation degree. Our present method can be applied to improvement of these properties for various oriented ceramics.

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