Effect of Fired Ag Electrodes on Electrical Properties of a $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ Single Crystal

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$\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ 単結晶の電気特性に及ぼす焼き付け銀電極の影響

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The dielectric constants and electromechanical coupling coefficients of $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ (PZNT91/9) single crystals with different electrode materials have been investigated. Two types of electrodes, sputtered Au/Ti and fired Ag, were applied to single crystals of PZNT91/9. The dielectric constant K at room temperature was 8000 for samples with Au/Ti electrodes. However, the sample with fired Ag electrodes had a lower K value of 1000. After electrical poling, the sample with Au/Ti electrodes had an electromechanical coupling coefficient k_t of 52.7%, while the sample with fired Ag electrodes showed a relatively high k_t value of 61.4%. This could be the result of the large amount of mechanical stress in the fired Ag electrode. Spontaneous intrinsic polarization of the rhombohedral system may be reoriented parallel or antiparallel along one particular direction because of the mechanical stress.

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1. Introduction

Lead-based ferroelectric perovskite compounds with the general formula $\text{Pb}(\text{B}'\text{B}'')\text{O}_3$ are applicable for use in capacitors, electrostrictive actuators and generators. The solid solutions of lead zinc niobate, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) and lead titanate, PbTiO_3 (PT), have a morphotropic phase boundary (MPB) near 9 mol% PT. The electrical properties of PZNT91/9 single crystals were reported by Kuwata et al. in 1982.¹⁾ The (001) plane crystal has an exceptionally large piezoelectric constant ($d_{33} > 1500$ pC/N) and electromechanical coupling coefficient ($k_{33} > 92\%$). Thus, these single crystals are expected to be applicable for use in high-quality ultrasonic transducers as replacements for conventional $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) ceramics. However, these excellent piezoelectric properties were measured using sputtered electrodes. Fired Ag electrodes are used for PZT ceramics due to their excellent soldering properties, reasonable cost and high reliability. However, the effects of fired Ag electrodes on the physical and electrical properties of PZNT91/9 single crystals have not been studied so far. The purpose of this study is to investigate the dielectric and electromechanical properties of PZNT91/9 single crystals with fired Ag electrodes along with those of sputtered Au/Ti electrodes.

2. Experimental details

The PZNT91/9 single crystals were prepared by the PbO flux method.¹⁾ The raw powders of PbO, ZnO, Nb_2O_5 and TiO_2 were mixed with a pestle and mortar, and the resulting mixture was calcined at 800°C for 2h in an Al_2O_3 sagger. The calcined powders were mixed with 6 % PVA solution. The result was pressed at 9.8×10^7 N/m² to produce pellets 37 mm in diameter and 10 mm thick. The pellets were sintered at 1000°C for 4h in a dense MgO crucible. A 55 mol% PZNT91/9 sintered pellet and 45 mol% PbO flux were placed in a 100 ml Pt crucible. The Pt crucible was heated to 1250°C for 4h and then cooled to 900°C at 0.5°C/h. The crucible was then air-quenched to room temperature over approximately 24h. The resulting PZNT91/9 single crystals were rhombohedral. The crystals

were cut along the pseudo-cubic (001) plane¹⁾ after the orientation was determined with a Laue X-ray diffraction pattern. The obtained wafer size was approximately $15 \times 15 \times 0.5$ mm³. Thin films of Au/Ti (=200 nm/50 nm) were formed by sputtering. This wafer was cut into samples $4 \times 4 \times 0.4$ mm³ with a dicing saw (Disco, DAD-2H/6T). After measuring the dielectric properties as a function of temperature increase, the samples were immersed in silicone oil and poled in a 1 kV/mm electric field. The electric field was applied at a temperature of 200°C for 15 min, and the samples were then cooled to 30°C in the electric field for approximately 3h. The electromechanical coupling coefficient, k_t , was measured using an impedance analyzer (HP-4195A; network mode) by the resonance and antiresonance frequency methods. The Au/Ti electrodes were then removed with #4000 sand paper. Commercially available Ag electrode paste (Shoei Chemical Co., Tokyo; H4190) was adhered to the samples by a screen printing method and then fired in air at 700°C for 5 min. The thickness of the Ag electrodes was 13 microns. After applying the Ag electrodes, the above process of dielectric measurement, poling and piezoelectric measurement was carried out. The microstructure of the cross section and the surface of the fired Ag samples was observed using a scanning electron microscope (SEM; JEOL JSM-T20).

3. Results and discussion

3.1 Microstructure and dielectric properties

Figure 1(a) shows a cross section of a PZNT91/9 sample with an Au/Ti electrode and, (b), with an Ag electrode. No additional phase²⁾ (such as pyrochlore or glass) is observed at the boundary of either sample between the electrode and the single crystal. Figure 2 shows the temperature dependence of dielectric constants and dissipation factors of samples with Au/Ti sputtered electrodes and with Ag electrodes after removal of the Au/Ti electrodes. Both the dielectric constant and the dissipation factor of the Au/Ti sputtered sample showed an anomaly at approximately 80°C (denoted as T_{FR} hereinafter), which corresponds to the rhombohedral-tetragonal phase change. The dielectric

Fig. 1. Cross section of the boundary area between (a) PZNT91/9 single crystal and Au/Ti electrode, and (b) between PZNT91/9 single crystal and Ag electrode.

constant of a sample with Ag electrodes decreases rapidly below the Curie temperature, T_C . Simultaneously, the dissipation factor increases from T_{FR} to T_C . These phenomena were found to be very similar to the behavior of BaTiO₃ (BT),³⁾ and the discussion of the mechanism behind this behavior follows.

3.2 Mechanism of dielectric constant decrease

The decrease in the dielectric constant of PZNT91/9 with Ag electrodes is very similar to that of a thermally poled BT single crystal.³⁾ The dielectric constant of PT⁴⁾ or BT³⁾ decreases when the proportion of the 90° domain is reduced by mechanical detwining⁴⁾ (or thermal poling³⁾); we refer to mechanical detwining⁴⁾ as "mechanical poling⁵⁾" in this paper. As a result of the mechanical poling, the proportion of the 180° domain increases. In other words, the ferroelectric phase of the ferroelectric material exhibits a very small dielectric constant as a result of the reduced 90°-domain. The decrease in dielectric constant of PZNT91/9 can be attributed to the same mechanism that is proposed for PT and BT. In PZNT91/9, mechanical poling is also expected to cause a decrease in the domains other than 180°. The Ag electrode shrinks to approximately 80% of its initial length, 64% of its initial area and 50% of its initial volume because the Ag paste is designed to correspond to

Fig. 2. Temperature dependence of (a) dielectric constant and (b) dissipation factor of PZNT91/9 single crystals with sputtered Au/Ti electrodes and fired Ag electrodes.

the amount of linear sintering shrinkage of approximately 80% for conventional ceramics. Consequently, single crystal samples were under compressive stress after the Ag electrodes were fired.

Because of the rhombohedral symmetry of PZNT91/9, there are four kinds of equivalent [111] polar directions (eight directions if polarities are accounted for) to which the polarization can spontaneously orient.⁶⁾ In the present case, the compressive stress forced the spontaneous polarization to rotate or reorient parallel or antiparallel along one particular direction. Accordingly, the amount of 71° (109°)-domains was decreased and 180°-domains became predominant.

The dielectric constant falls as a result of the decrease in the amount of 71° domain. However, no phase transition is observed at T_{FR} . If such a phase transition occurred, the dielectric constant would have increased at T_{FR} ,⁷⁾ accompanied by a decrease in the dissipation factor. The experimental result shows that there is no phase transition to tetragonal at T_{FR} , which may be due to inner stresses that are caused by Ag electrodes. In other words, it can be assumed that T_{FR} and T_C coincide at this level of stress. Therefore, the dissipation factor peak (at T_C) increases compared with that of the Au/Ti sputtered sample. The dielectric constant also increases slightly at T_C .

The present mechanism has been deduced only from changes in the dielectric constant and the dissipation factor. A clearer mechanism will be proposed in the future.

3.3 Electromechanical coupling factor, k_t

For mechanically poled PZNT91/9 with Ag electrodes,

Table 1. Comparison of PZNT91/9 with Fired Ag Electrodes and Au/Ti Sputtered Electrodes

	fired Ag electrodes	sputtered Au/Ti electrodes
thickness (μm)	13	0.25
dielectric constant @20°C	1000	8000
dielectric constant @Curie temp.	59000	59000
dissipation factor @20°C (%)	3.0	4.0
dissipation factor @ Curie temp. (%)	8.3	2.2
electromechanical coupling coefficient, k_t (%)	61.4	52.7

electrical poling is easier than with the Au/Ti sputtered electrodes because the 180° domain, which more mobile than the 71° domain, is already predominant.

Table 1 and Fig. 3 show k_t values for samples with Ag electrodes and sputtered electrodes. Samples with fired Ag electrodes have a much larger k_t ($=61.4\%$) than those of the samples with sputtered Au/Ti electrodes ($=52.7\%$).

4. Summary

Two types of electrodes, sputtered Au/Ti and fired Ag, were applied to $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ (PZNT91/9) single crystals and showed the results obtained below. These results suggest at a new method for controlling the domain structure and electrical properties of these crystals.

(1) The dielectric constant K at room temperature is 8000 for Au/Ti electrode samples. However, samples with fired Ag electrodes indicate the lower K value of 1000.

(2) The dielectric constant K_{max} at the Curie temperature is almost the same for both types of electrodes.

(3) After electrical poling, Au/Ti samples indicate an electromechanical coupling coefficient k_t of 52.7%, while samples with fired Ag electrodes have a relatively high k_t value of 61.4%.

(4) The lower dielectric constant in the case of the fired Ag electrodes may be due to mechanical poling. This phenomenon increases the mechanical coupling factor k_t of

$$k_t^2 = 0.405f_r/(f_a - f_r) + 0.810$$

f_r : resonance frequency

f_a : anti-resonance frequency

$$\text{a) } k_t = 52.7(\%) \quad \Delta f = 0.70(\text{MHz})$$

$$\text{b) } k_t = 61.4(\%) \quad \Delta f = 0.95(\text{MHz})$$

$$\Delta f = f_a - f_r$$

Fig. 3. Impedance properties of PZNT91/9 with (a) sputtered Au/Ti electrodes and (b) fired Ag electrodes.

poled single crystals.

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