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Crystal Orientation Dependence and Aging of Giant Electromechanical Coupling Factor of k_{31} Mode and Piezoelectric d_{31} Constant in $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ Single Crystals

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Abstract: The $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ single crystals with various crystal orientations were evaluated regarding k_{31} and d_{31}. These values depended on their crystal orientations. The dielectric constant (ε_r) increased with the time in the crystal of (110) orientation, while the ε_r's of the crystals with (100) and (111) orientations were almost constant. The poling field and bipolar pulse field dependences of k_{31} and d_{31} were also investigated. The giant k_{31} and d_{31} were obtained in the crystal of (100) orientation by the pulse poling as well as by DC poling.
Key words: giant electromechanical coupling factor of k_{31} mode, giant piezoelectric d_{31} constant, lead zinc niobate titanate single crystal, crystal orientation dependence, aging

1. INTRODUCTION

Ferroelectric single crystals made of compounds such as $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZNT91/09) have been attracting considerable attention, because of the large electromechanical coupling factor of the k_{33} mode of over 92 % [1]. Since high-quality and large crystals are necessary to develop devices such as transducers for medical use [2], the fabrication of PZNT91/09 single crystals with large dimensions have been undertaken and succeeded in [3]. Recently, we found the giant electromechanical coupling factor of k_{31} mode over 80% and piezoelectric d_{31} constant nearly -1700 pC/N in ferroelectric single crystals composed of PZNT91/09 poled along [001] of the original cubic direction [4, 5]. The discovery of the giant k_{31} and d_{31} constant would become a breakthrough in the applications to high performance sensors and actuators utilizing a large k_{31} (d_{31}) mode as well as the devices utilizing a large k_{33} (d_{33}) mode. In this study, we evaluate the piezoelectricity of our large PZNT91/09 single crystals, focusing on particularly the crystal orientation dependence and aging of the k_{31} (d_{31}) mode. Furthermore, we measure the poling field and bipolar pulse field dependences of the ferroelectric properties such as k_{31} and d_{31} to estimate their domain structures.

2. EXPERIMENTAL

The PZNT91/09 single crystals with the dimensions of 50 mm (2 inches) diameter, 35 mm height, and 325 g weight were grown by the solution Bridgman method [3]. The as-grown single crystals were cut along [001], [110] and [111] of the original cubic direction confirmed by X-ray diffraction (XRD) and from Laue photographs. The single-crystal samples with dimensions of 4.0^Wx13^Lx0.36^T mm for k_{31}, k_t and d_{31} were prepared to evaluate the crystal orientation, poling field and bipolar pulse field dependences of the ferroelectric properties and their aging. Gold electrodes for the following DC field applying and pulse field applying, and electrical measurements were fabricated by conventional sputtering. DC poling was conducted at 40℃ for 10 min by applying 1.0 kV/mm to obtain resonators with various crystal orientations. Poling field dependence was measured while varying the poling field (E) from 0 → 100 → 150 → --- 1000 → --- 2000 V/mm at 40℃ for 10 min [6]. Bipolar triangle pulse with the period of 800 ms were applied while varying the bipolar pulse field (E) from 0 → 200 → 300 → --- 1000 → --- 2000 V/mm at 40, 80 and 120℃. After each applying the field, the dielectric and piezoelectric properties were measured at room temperature using an LCR meter (HP4263A), an impedance/gain-phase analyzer (HP4194A) and a d_{33} meter (Academia Sinica: ZJ-3D).

3. RESULTS AND DISCUSSION

3.1 Crystal Orientation and Poling Field Dependences

Table I shows the ferroelectric properties before and after poling in PZNT91/09 single crystals with various crystal orientations. The k_{31} and d_{31} depended on the crystal orientations. Furthermore, there were fluctuations of dielectric constant (ε_r) before and after poling, k_{31} and d_{31}, even though the crystal orientation was the same. It was thought that the difference in these values was due to the difference in their domain structures. The giant k_{31} and d_{31} could be obtained in the case of the (100) crystal poled along [001] of the original cubic direction. From the poling field dependence of ferroelectric properties, there was little fluctuation of k_t (thickness vibration mode) and fc_t (frequency constant of k_t mode) regarding the (110) crystals while there were great fluctuation of ε_r, k_{31} and fc_{31}. This means that the domain structures in thickness (the direction parallel to the poling field) are almost the same; however, those in the direction perpendicular to the poling field (4.0^Wx13^L mm) are quite different.

Table I. Ferroelectric properties before and after poling in PZNT91/09 single crystals with various crystal orientations.

No.	Orien-tation	Before poling		After poling*							
		tanδ (%)	ε_r	tanδ (%)	ε_r	k_{31} (%)	k_t (%)	d_{31} (pC/N)	d_{33} (pC/N)	fc_{31} (Hz·m)	fc_t (Hz·m)
1	(100)	3.83	2932	0.96	4186	79.1	54.8	-1476	2400	569	2094
2	(110)	3.78	4410	2.09	3512	59.0	38.8	-715	530	800	2309
3	(110)	4.50	3666	4.29	4755	30.3	37.1	-301	1030	1141	2334
4	(111)	3.29	4101	0.80	5934	-**	52.3	-	560	-	2455
5	(111)	3.02	3849	0.89	1606	18.9	38.7	-167	190	744	2468

* Poling conditions; temperature: 40℃, time: 10 min, E: 1.0 kV/mm.

** Weak impedance response not to calculate k_{31}.

3.2 Aging Characteristics

Figures 1 (a) ~ (c) shows the aging characteristics for ε_r, k_{31} and fc_{31} (frequency constant of k_{31} mode) vs time, respectively. Although the ε_r's of (100) and (111) crystals became constant with time, the ε_r's of (110) crystals increased with time and both the values reached to a constant of 6,000 in Fig. 1 (a). Therefore, it is said that the domain structures of the (110) plane (4.0^Wx13^L mm) after poling change into a stable state with time. The same tendencies were observed in the cases of k_{31} vs time (Fig. 1 (b)) and fc_{31} vs time (Fig. 1 (c)). The giant k_{31} and d_{31} with excellent aging characteristics can be archived in the (100) crystal poled along [001] of the original cubic direction. In addition, the lowest fc_{31} below 600 Hz·m, which is obtained in the (100) crystals (Fig. 1 (c)), accompanied giant k_{31} over 80%.

3.3 Pulse Field Dependence

P-E hysteresis loops of the (100) crystal were measured by bipolar triangle pulse. Figures 2 (a) and (b) show the bipolar pulse field (E) dependence of the remanent polarization (Pr) and coercive field (Ec) at various measurement temperature of 40 ℃ (rhombohedral phase in PZNT91/09), 80℃ (M.P.B.) and 120℃ (tetragonal phase). The threshold of E vs Pr decreased with increasing the measurement temperature and the maximum Pr's were obtained at 80℃ (Fig. 2 (a)). On the other hand, the Ec increased with decreasing the measurement temperature and the maximum Ec region was the E's over 1,500 V/mm at 40℃. It was thought the higher Ec was needed to achieve mono-domain crystal in the direction perpendicular to the polling field (4.0^Wx13^L mm).

3.4 Comparison between DC Poling and Bipolar Pulse Poling

After each applying the bipolar triangle pulse, the ferroelectric properties were measured to evaluate the pulse poling in the case of the (100) crystal poled along [001] direction. Figures 3 (a) ~ (c) show the DC poling field and bipolar pulse poling field (E) dependences of ε_r, k_{31} and fc_{31} in the temperature of 40℃. Both the ε_r's show the three stages in ε_r vs E, and further, the stages in ε_r move to higher E in the case of the pulse poling (Fig. 3 (a)). The giant k_{31} was obtained in higher E in the cases of the pulse poling in comparison with the DC poling (Fig. 3(b)). The lowest fc_{31} was observed in the same stage obtained the giant k_{31} (Fig. 3 (c)). Therefore, it is said that the giant k_{31} and d_{31} appear to apply the sufficient poling field to realize mono-domain crystal in the direction perpendicular to the poling [5].

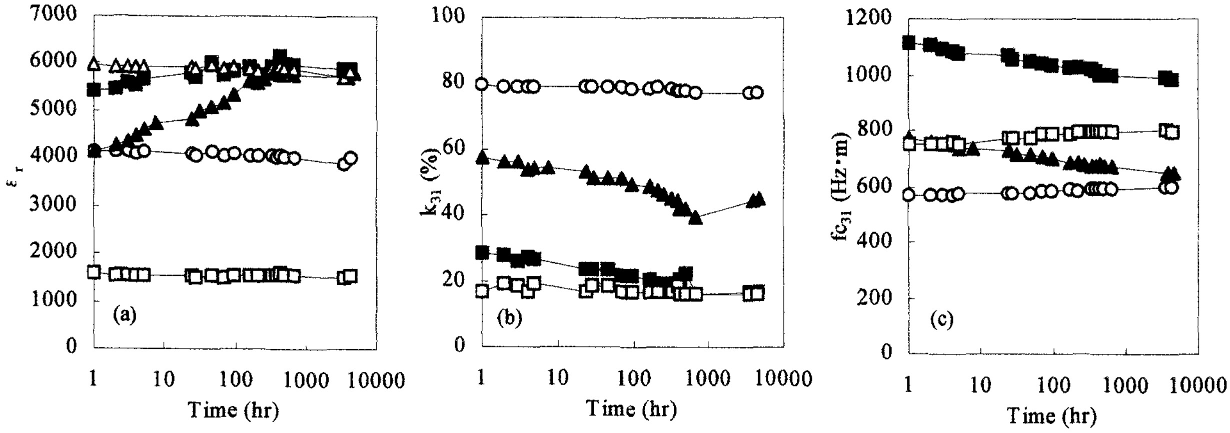

Fig. 1. Aging characteristics for (a) ε_r, (b) k_{31} and (c) fc_{31} vs time in (100) crystal (No. 1: ○), (110) crystals (No. 2: ▲, No. 3: ■) and (111) crystals (No. 4: △, No. 5: □).

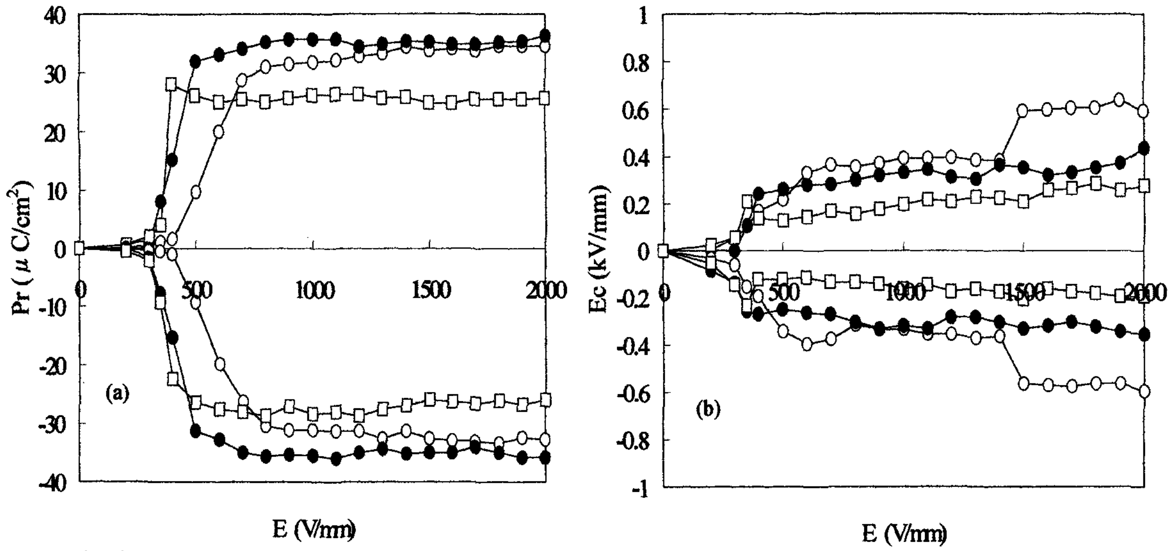

Fig. 2. Bipolar pulse field (E) dependence of (a) remanent polarization (Pr) and (b) coercive field (Ec) at measurement temperatures of 40℃ (○), 80℃ (●) and 120℃ (□) in (100) crystals.

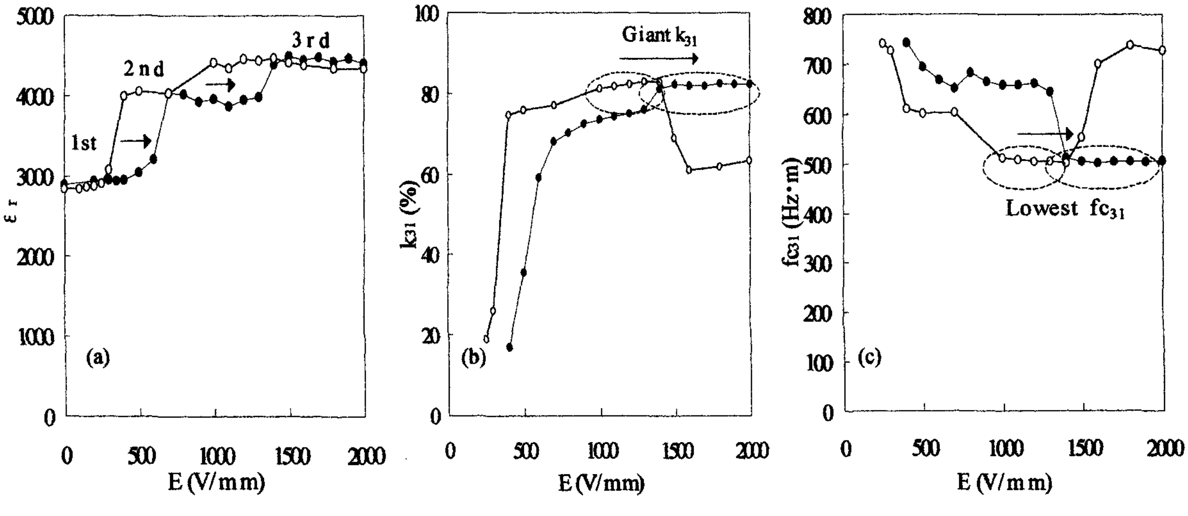

Fig. 3. DC poling field (○) and bipolar pulse poling field (●) dependences of (a) ε_r, (b) k_{31} and (c) fc_{31} at poling temperature of 40℃ in (100) crystals.

4. SUMMARY

Giant k_{31} and d_{31} in PZNT91/09 single crystal could be obtained in the cases of ① the DC poled and bipolar pulse poled (100) crystal along [001] of the original cubic direction, ② the poling temperature of 40℃ in the rhombohedral phase of PZNT91/09 and ③ the sufficient poling field to realize mono-domain crystal in the direction perpendicular to the poling field.

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