Transactions of the Materials Research Society of Japan 30[1] 83-86 (2005)

Impedance Response Analysis of Domain Structures in $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ Single Crystal with Giant k_{31}

Toshio Ogawa
Department Electrical, Electronics and Information Engineering
Shizuoka Institute of Science and Technology, 2200-2 Toyosawa, Fukuroi, Shizuoka 437-8555, Japan
Fax: 81-538-45-0110, e-mail: ogawa@ee.sist.ac.jp

Frequency responses of impedance to 500 kHz in $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZNT91/09) single-crystal plates (13^Lx4^Wx0.36^T mm) were analyzed on the two kinds of the length extensional vibration modes of k_{31} (13^L mm) and k_{32} (4^W mm). It was found that there were two (low and high) frequency constants (fc) of 520 kHz-m and 830 kHz-m on these modes. The response with the giant k_{31} over 80% has the low fc on k_{31} mode and the high fc on k_{32} mode which are caused by the anisotropy of the crystal symmetry. It was thought that the crystal structure with the giant k_{31} was transformed into a new phase such as monoclinic phase different from rhombohedral and tetragonal phases. Therefore, the giant k_{31} appeared in the case of the low symmetry phase, which can be realized the single-domain structure in the single-crystal plates.

Key words: giant k_{31}, $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ single crystal, impedance response, domain structure, crystal anisotropy

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 attention, because of the large electromechanical coupling factor of the k_{33} mode of over 92 % [1]. However, the coupling factors of the k_{31} mode were 49%-62% in (100) plane PZNT91/09 single crystals [1-3]. Recently, we found the giant k_{31} over 80% and piezoelectric d_{31} constant nearly -1700 pC/N in the crystals [4]. The origin of the giant k_{31} and d_{31} constant was due to realize single-domain structure in the direction perpendicular to the poling field as well as in the direction parallel to the poling field [5]. It was clarified that the giant k_{31} and d_{31} could be obtained in the cases of; (1) the 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 single-domain crystal [6]. In addition, the relationship between the sample dimensions and the direction of the vibration mode was significant to obtain these giant values. Therefore, we evaluated the anisotropy between k_{31} and k_{32} modes and their frequency constants in the single-crystal plates.

2. EXPERIMENTAL PROCEDURE

The PZNT91/09 single crystals with the dimensions of 50 mm (2 inches) diameter, 35 mm height, and 325 g weight were grown by a solution Bridgman method [7]. The as-grown single crystals were cut along of the original cubic direction confirmed by X-ray diffraction and from Laue photographs. (100) plane single-crystal plates with dimensions of 13^Lx4.0^Wx0.36^T mm for k_{31} and k_t (thickness vibration mode of the plate) were prepared to evaluate the piezoelectric properties. Gold electrodes for the following DC field applying and electrical measurements were fabricated by conventional sputtering. DC poling was conducted at 40℃ for 10 min by applying E=1.0~3.0 kV/mm to obtain the plate (13^Lx 4.0^W mm) resonators. After each applying the DC poling field parallel to the thickness of the plate (0.36 mm), the frequency responses of impedance to 500 kHz were measured at room temperature using an impedance /gain-phase analyzer (HP4194A).

3. RESULTS AND DISCUSSION

3.1 Frequency responses to 500 kHz

Three PZNT91/09 single-crystal plates of Nos. 1-3 with dimensions of 13^Lx4.0^Wx0.36^T mm were prepared through the different poling and annealing processes (for example, No. 1-1 → --- → No. 1-6 in the sample No. 1) in Table I. The annealing over the Curie temperature of 175℃ (200℃) for 30 min were carried out to depolarize the samples. After each poling, the impedance responses of PZNT91/09 single-crystal plates were analyzed according to the vibration modes and frequency constants of fc_{31} and fc_{32} on k_{31} and k_{32} (Fig. 1) such as the fundamental vibration and their overtones. Since the plates after poling had the values of k_t of 54-60%, it was confirmed that they were fully poled in the direction of the thickness. Figure 2 shows the frequency responses of impedance to 500 kHz and their values of k_{31} in the case of No. 1-1~6 in Table I. The annealing over the Curie temperature (200℃) for 30 min were carried out to depolarize the samples between No. 1-1 and No. 1-2. There were two kinds of frequency constants (fc); high (830 Hz-m) and low (520 Hz-m). In the cases of k_{31}=40~43% (Figs. 2 (a), (c) and (f)), we could observed the high fc (□) on k_{31} mode and the low fc (•) and high fc (■) on k_{32} mode. In k_{31}=50~56% (Figs. 2(b) and (e)), the high fc on k_{31} (□) and k_{32} (■) modes were only found. In k_{31}=80% (Fig. 2(d)), which corresponds to a giant k_{31}, the low fc on k_{31} (○) and k_{32} (•) modes in addition to the high fc (■) on k_{32} mode were observed.

Table I Poling and annealing processes for PZNT91/09 single-crystal plates.

Sample No.	E (kV/mm)
1-1	1.0
	Annealing
1-2	1.0
1-3	1.5
1-4	2.0
1-5	2.5
1-6	3.0
2-1	1.0
	Annealing
2-2	1.0
2-3	1.5
3-1	1.0

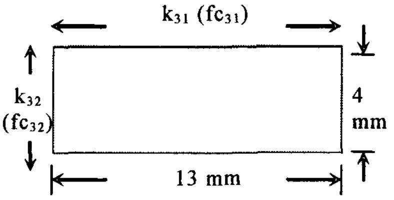
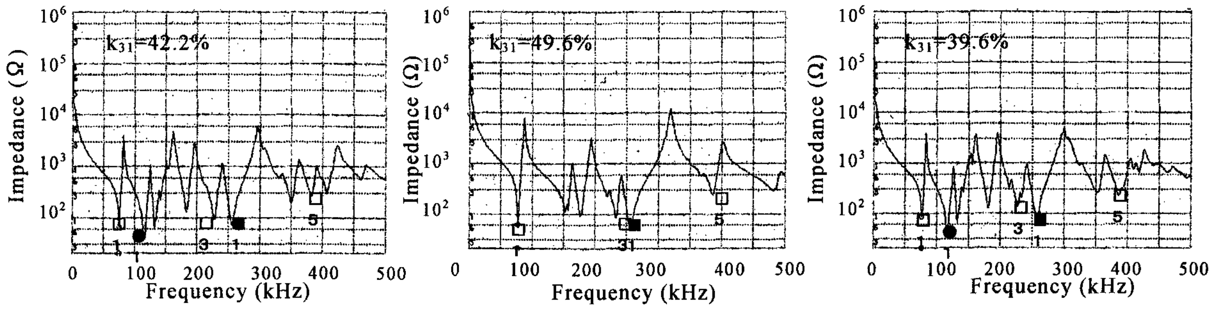
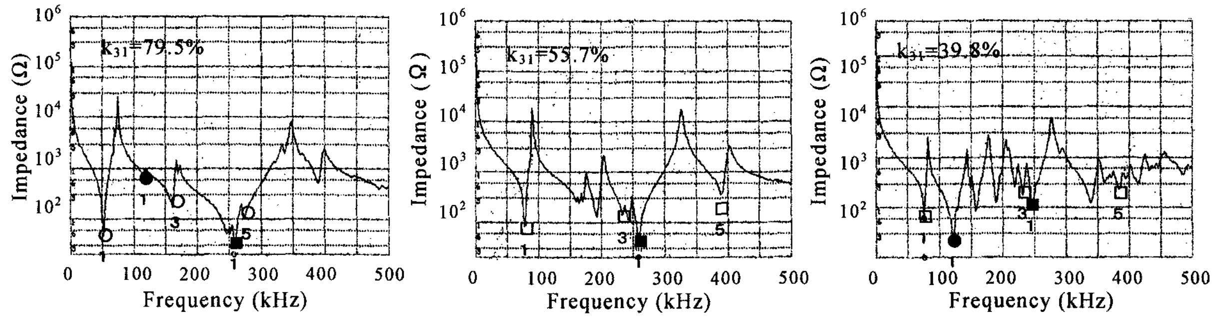


Fig. 1 Relationships between dimensions of PZNT91/09 single-crystal plates, vibration modes and frequency constants (fc_{31} and fc_{32}) on k_{31} and k_{32}; the thickness of the plate is 0.36 mm.

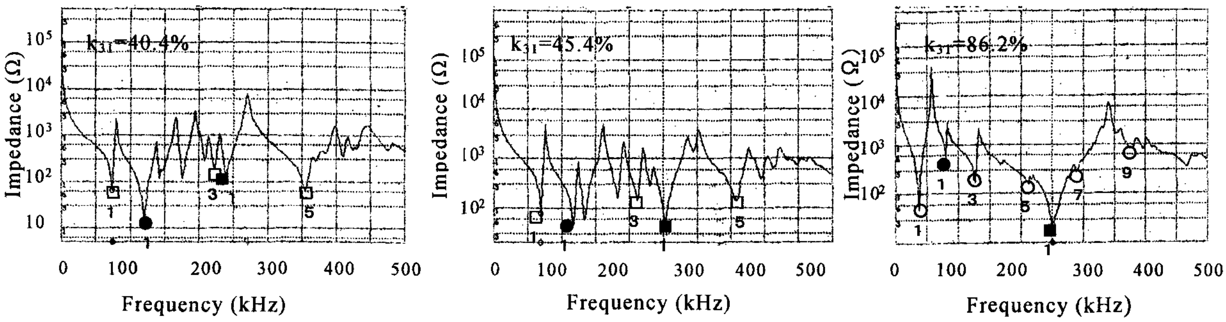


(a) No. 1-1 (E=1.0kV/mm) (b) No. 1-2 (E=1.0 kV/mm) (c) No. 1-3 (E=1.5 kV/mm)



(d) No. 1-4 (E=2.0 kV/mm) (e) No. 1-5 (E=2.5 kV/mm) (f) No. 1-6 (E=3.0 kV/mm)

Fig. 2 Frequency responses of impedance in PZNT91/09 single-crystal plates with different k_{31}: Sample No. 1-1~6 (□1/ ○1: k_{31} fundamental, □3/ ○3: k_{31} 3rd overtone, □5/ ○5: k_{31} 5th overtone, ■1/ ●1: k_{32} fundamental mode).



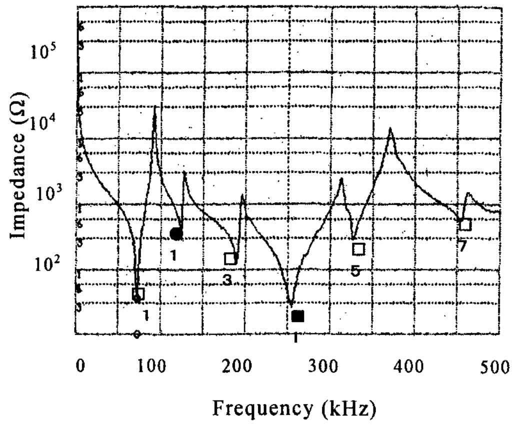
(a) No. 2-1 (E=1.0 kV/mm) (b) No. 2-2 (E=1.0 kV/mm) (c) No. 2-3 (E=1.5 kV/mm)

Fig. 3 Frequency responses of impedance in PZNT91/09 single-crystal plates with different k_{31}: Sample No. 2-1~3 (□1/ ○1: k_{31} fundamental, □3/ ○3: k_{31} 3rd overtone, □5/ ○5: k_{31} 5th overtone, ○7: k_{31} 7th overtone, ○9: k_{31} 9th overtone, ■1/ ●1: k_{32} fundamental mode).

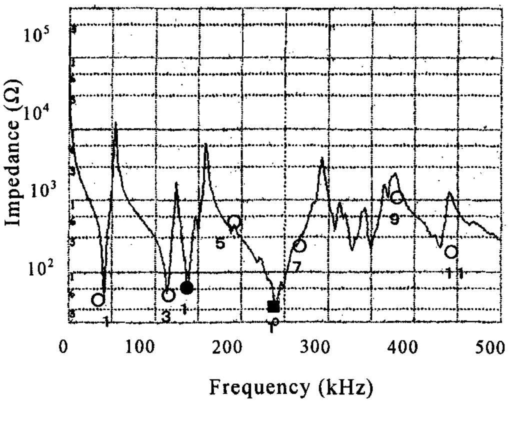
Figure 3 shows the frequency responses in the cases of No. 2-1~3 in Table I. In k_{31}=41~46% (Figs. 3(a) and (b)), the high fc (□) on k_{31} mode and the low fc (●) and high fc (■) on k_{32} modes were confirmed. In a giant k_{31} of 86.2% (Fig. 3(c)), the low fc on k_{31} (○) and k_{32} (●) modes in addition to the high fc (■) on k_{32} mode were confirmed.

3.2 Frequency responses in giant k_{31}

Figure 4 shows the frequency responses just before (Fig. 4(a)) and after realizing a giant k_{31} (Fig. 4(b)). Both the responses have the low fc (●) and high fc (■) on k_{32} mode. The differences between two responses were the high fc (□) (Fig. 4(a)) or the low fc (○) (Fig. 4(b)) on k_{31} mode, respectively. From the investigating various kinds of impedance responses including above mentioned, we summarized the relationships between k_{31}, the low fc and high fc on k_{31} and k_{32} modes to realize the giant k_{31}>80% in Fig. 5.



(a) k_{31}=68.0%



(b) k_{31}=70.8%

Fig. 4 Frequency responses of impedance in PZNT91/09 single-crystal plates with k_{31} nearly 70% (□1 /○1: k_{31} fundamental, □3/ ○3: k_{31} 3rd overtone, □5/ ○5: k_{31} 5th overtone, □7/ ○7: k_{31} 7th overtone, ○9: k_{31} 9th overtone, ○11: k_{31} 11th overtone, ■1/ ●1: k_{32} fundamental mode).

In k_{31}=40~45% (Figs. 5(a) and (b)), the low fc (●) on k_{32} mode was observed in addition to the high fc on k_{31} (□) and k_{32} (■) modes, which corresponds to the responses of k_{31}=50~57% (Figs. 5(c), (d)). The response with the giant k_{31} has only the low fc (○) on k_{31} mode and the high fc (■) on k_{32} mode (Fig. 5(e)), which results from the anisotropy in the plate sample. Therefore, it was found from the results of the impedance response analysis that the way to realize the giant k_{31} needed the processes to produce the low fc (●) on k_{32} mode in the PZNT91/09 single-crystal plates.

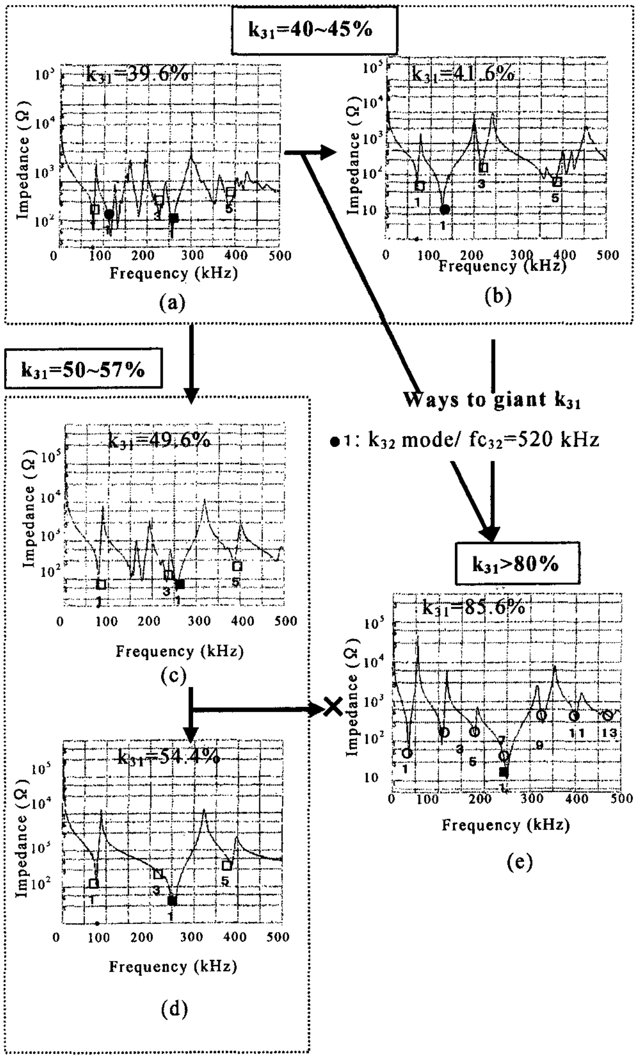


Fig. 5 How can be realized giant k_{31}? Classification regarding impedance responses on k_{31} and k_{32} modes in PZNT91/09 single-crystal plates; (□1/ ○1: k_{31} fundamental, □3/ ○3: k_{31} 3rd overtone, □5 / ○5: k_{31} 5th overtone, ○7: k_{31} 7th overtone, ○9: k_{31} 9th overtone, ○11: k_{31} 11th overtone, ○13: k_{31} 13th overtone, ■1/ ●1: k_{32} fundamental mode). The impedance response of (e) in this figure corresponds to the PZNT single-crystal plate of the sample No. 3-1 in Table I.

3.3 Anisotropy of crystal phase in giant k_{31}

Figure 6 shows the relationships between k_{31}, anisotropy, frequency constant (fc_{31} and fc_{32}) and crystal phase in PZNT91/09 single crystals. The k_{31} dependence of crystal phase could be explained by the anisotropy of the fc on k_{31} and k_{32} modes. In k_{31}=50~57%, a typical frequency response was observed in Fig. 5(d); this means tetragonal phase (a=b≠c in Fig. 6).

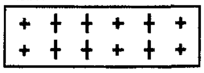
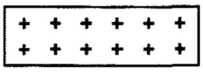
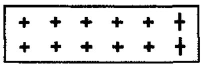
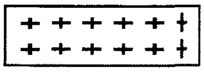
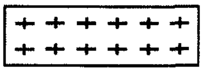
k_{31} (%)	Anisotropy	Frequency constant (Hz·m)	Phase
40~ 45		$fc_{31}=fc_{32}$ =830 (+) fc_{32}=520 (|)	Rhombohedral (a=b=c)
50~ 57		$fc_{31}=fc_{32}$ = 830 (+)	Tetragonal (a=b≠c)
68		$fc_{31}=fc_{32}$ =830 (+) fc_{32}=520 (|)	Tetragonal (a=b≠c)
70~ 80		fc_{31}=520 (—) fc_{32}=830 (|) fc_{32}=520 (|)	New phase (a≠b≠c)
>80		fc_{31}=520 (—) fc_{32}=830 (|)	New phase (a≠b≠c)

Fig. 6 Anisotropy of (100) plane PZNT91/09 single-crystal plates: Relationships between k_{31}, anisotropy of frequency constant and crystal phase.

On the other hand, a typical frequency response was observed in Fig. 5(e) in the case of k_{31}>80%; that means to produce a new phase (a≠b≠c in Fig. 6) such as monoclinic phase different from the tetragonal phase. Therefore, that is to say, the giant k_{31} can be obtained in the new phase to control by the process combination of the poling and annealing in Table I.

4. CONCLUSIONS

From the investigation of the frequency responses of impedance to 500 kHz in great detail, the anisotropy on k_{31} and k_{32} modes was clarified. They can be explained by the reorientation for their frequency constants of fc_{31} and fc_{32}. The giant k_{31} appeared in a new phase such as monoclinic phase different from rhombohedal and tetragonal phases. This phase can be realized single-domain structure in the plate with giant k_{31} over 80%.

5. ACKNOWLEDGMENTS

This work was partly supported by a Grant-in-Aid for Scientific Research (C) (No. 12650327) from the Ministry of Education, Culture, Sport, Science and Technology, the Foundation from the Regional Science Promotion (RSP) program of the Japan Science and Technology Agency and the Murata Science Foundation. The authors would like to thank the Research Laboratory of JFE Mineral Co., Ltd. for supplying the single-crystal plates.

6. REFERENCES

[1] J. Kuwata, K. Uchino and S. Nomura, *Jpn. J. Appl. Phys.*, **21**, 1298 (1982).

[2] J. Yin, B. Jiang and W. Cao, *IEEE Proc. Medical Imaging*, **3664**, 239 (1999).

[3] J. Yin, B. Jiang and W. Cao, *IEEE Trans. Ultrason. Ferroelec. Freq. Contr.*, **47**, 285 (2000).

[4] T. Ogawa, Y. Yamauchi, Y. Numamoto, M. Matsusita and Y. Tachi, *Jpn. J. Appl. Phys.*, **41**, L55 (2002).

[5] T. Ogawa and Y. Numamoto, *Jpn. J. Appl. Phys.*, **41**, 7108 (2002).

[6] T. Ogawa, *Ferroelectrics* , in press.

[7] M. Matsushita, Y. Tachi and K. Echizenya, *Abstract of Am. Ceram. Soc. 103rd Annual Meeting*, (2001) p. 247.

(Received December 23, 2004; Accepted January 31, 2005)