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# Pressure dependence of piezoelectric properties of a $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ binary system single crystal near a morphotropic phase boundary

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**Abstract**

The piezoelectric properties of a $Pb[(Mg_{1/3}Nb_{2/3})_{0.68}]Ti_{0.32}O_3$ binary system single crystal poled along the [001] direction in the rhombohedral phase were investigated under pressures up to 400 MPa at 25 °C. For the transverse electromechanical property, the difference $\Delta f$ between the resonance $f_r$ and antiresonance frequencies $f_a$, the $\Delta f/f_r$ and the electromechanical coupling coefficient $k_{31}$ value in the $k_{31}$ mode with hydrostatic pressure ($p$) became smaller because of the increase in $f_r$ and the almost constant $f_a$ with $p$. The $k_{31}$ value decreased by 16% at 400 MPa. On the other hand, for the longitudinal electromechanical property, the $\Delta f$, the $\Delta f/f_r$ and the $k_{33}$ value in the $k_{33}$ mode with $p$ remained almost constant because of the almost constant $f_r$ and $f_a$ with $p$. The changes in the values of the elastic compliances $s_{11}^E$ and $s_{33}^E$ with $p$ were found to be large from the changes in $f_r$ and $f_a$ with $p$. $s_{11}^E$ and $s_{33}^E$ at 400 MPa were estimated to be 35.4 and 75.1 $\times 10^{-12}$ m$^2$ N$^{-1}$, respectively. A mechanical quality factor $Q$ almost constant with $p$ in the $k_{33}$ mode in contrast to the large decrease in $Q$ in the $k_{31}$ mode with $p$ in the pressure range up to 200 MPa was observed. A $k_{33}$ value almost constant with $p$ is considered, on the basis of the engineered domain concept, to be due to the stable domain configuration responsible for the longitudinal $k_{33}$ mode. Furthermore, the superior piezoelectric properties of the rhombohedral [001] single crystal in the vicinity of the morphotropic phase boundary composition were recently pointed out to come from the large shear piezoelectric constant $d_{15}$ of their single domain property. The hydrostatic pressure cannot influence the piezoelectric properties from the viewpoint of the contribution of the large shear mode $d_{15}$, since the uniform pressure introduces no shearing stresses. Consequently, the $k_{33}$ value measured for the $k_{33}$ mode remained almost constant with $p$ in the measured pressure range.

## 1. Introduction

Considerable attention has been given to single crystals of solid solutions of lead-based complex perovskite $Pb(B, B')O_3$ relaxor ferroelectrics–normal ferroelectric $PbTiO_3$ (PT) systems near the morphotropic phase boundary (MPB) for applications in ultrasonic, nondestructive testing (NDT) and actuator devices because of their superior piezoelectric properties compared to those of ceramics [1–5]. The $Pb[(Mg_{1/3}Nb_{2/3})_{0.68}]Ti_{0.32}O_3$[PMNT(68/32)] single crystal has been known to show a large piezoelectric constant ($d_{33}$ of over 1500 pC $N^{-1}$) and electromechanical coupling factor in the longitudinal bar mode ($k_{33}$ of over 90%), along the [001] axis in the rhombohedral phase [2–4, 6, 7]. Such enhanced electromechanical properties in the near-MPB compositions were known to be interpreted in terms of the engineered domain structures, where the ferroelectric domain wall structure is stabilized by the oblique electric field, that is, the [001] electric field for the rhombohedral phase (all refer to the cubic coordinates) [2, 4–8]. Recently, superior piezoelectric properties were reported [9, 10] to come from both the lattice effect of the large shear mode of $d_{15}$ and the multi-domain effect. We have reported previously [11, 12] the pressure dependence of the electromechanical coupling factors in the $k_{31}$ mode and the $k_{33}$ mode for the $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}]Ti_{0.09}O_3$ [PZNT(91/9)] single crystal. On the other hand, the effect of pressures on piezoelectric properties of ceramics was investigated in the pressure range up to 100 MPa, and a slight increase in piezoelectric constants and electromechanical coefficients with pressure was previously reported [13, 14]. In this paper, the hydrostatic pressure dependence of the electromechanical coupling factors in the $k_{31}$ mode and the $k_{33}$ mode for the [PMNT(68/32)] single crystal are presented.

## 2. Experimental procedure

PMNT(68/32) single crystals were obtained by a conventional solution Bridgman method [15–17]. The Ti concentration of the solid solution single crystals obtained was confirmed by inductive charge plasma (ICP) analysis [18]. The as-grown single crystals were cut along the pseudocubic [001] direction confirmed by x-ray diffraction and from Laue photographs. Multi-domain structures were observed by optical polarizing microscopy [19, 20]. The single crystal plate with dimensions of $4.00^w$ mm × $1.23^l$ mm × $0.33^t$ mm for the measurement of the $k_{31}$ ($d_{31}$) mode and the single crystal bar with dimensions of $2.50^w$ mm × $2.50^l$ mm × $7.50^t$ mm for the measurement of the $k_{33}$ ($d_{33}$) mode were prepared from a (001) crystal. Gold electrodes were deposited by conventional sputtering. The electrical capacitance and dielectric loss tangent, $\tan\delta$, were measured using an $LCR$ (inductance, capacitance, resistance) meter (HP-4154A) at 1 kHz. The specimens were poled in a 10 kV $cm^{-1}$ electric field at 40 °C for 15 min in an insulating liquid, silicone oil, to prevent arc. The electromechanical coupling factors were measured by the resonance and antiresonance frequency method using an impedance gain phase analyser (HP-4194A; network mode) [21]. The pressure apparatus used to apply hydrostatic pressures to the specimens was a simple intensifier-type press with Fluorinert as a pressure-transmitting fluid [22]. A suspension system of the hanging electrode type for the sample holder was adopted for the resonance measurement under pressure. The pressure dependence of resonance and antiresonance

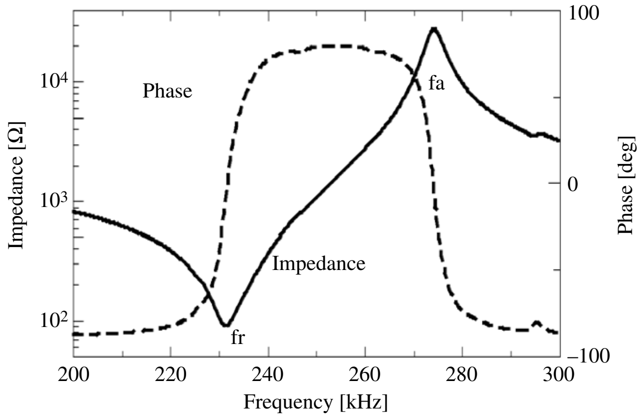


**Figure 1.** Resonance ($f_r$) and antiresonance ($f_a$) frequency characteristics of impedance and phase for the PMNT(68/32) single crystal oriented along the [001] axis in the $k_{31}$ mode at atmospheric pressure at 25 °C.

frequencies was measured during an increasing pressure run, and the pressure dependence of the electromechanical coupling factor $k$ was normalized with the value at 0 MPa (denoted as $k(0)$) as follows: $k/k(0)$. The piezoelectric constants $d$ were measured using a strain meter (Millitron No 1240).

## 3. Results

### *3.1. Transverse electromechanical properties*

The resonance and antiresonance frequency characteristics of the impedance and phase for the PMNT(68/32) single crystal oriented along the [001] axis in the $k_{31}$ mode in the rhombohedral phase were measured at 25 °C at atmospheric pressure and are shown in figure 1. The specimen had an electromechanical coupling coefficient of $k_{31} = 62.8\%$ in the $k_{31}$ mode in the [001] poled single crystal plate. The piezoelectric constant $d_{31}$ was estimated to be $-823$ pC $N^{-1}$ at atmospheric pressure. The relative permittivity $\varepsilon_r$ and $\tan\delta$ were measured to be 4083 and 0.29%, respectively, at 1 kHz at 25 °C in atmospheric pressure. These values were compared with $k_{31} = 59\%$, $d_{31} = -1330$ pC $N^{-1}$ [7], $\varepsilon_r = 4233$, and $\tan\delta = 0.9\%$ [6] for PMNT(67/33) and 48.6%, $-920$ pC $N^{-1}$ and $\varepsilon_r = 7800$ for PMNT(70/30) [23], reported previously. The scattering seen in these values in the vicinity of the MPB composition may be due to the multi-domain structure created by poling a crystal along a nonpolar direction [10] and some $TiO_2$ distributions within [001] specimens [18]. In order to clarify the change in the electromechanical coupling coefficient $k_{31}$ with pressure, the resonance and antiresonance frequency characteristics of the impedance and phase for the PMNT(68/32) single crystal were measured under various pressures up to 400 MPa at 25 °C. Figure 2 shows the resonance and antiresonance frequency characteristics of the impedance and phase for the PMNT(68/32) single crystal oriented along the [001] axis in the $k_{31}$ mode in the rhombohedral phase for various pressures. The electrical reflection within the pressure chamber was found to be suppressed due to the decrease in electrical sensitivity of the specimen element with pressure by increasing applied hydrostatic pressures [14]. With increasing pressure, the following noteworthy features were observed. (1) A change of the resonance and antiresonance frequency characteristic curves from sharp to broad ones was observed. (2) The resonance frequency

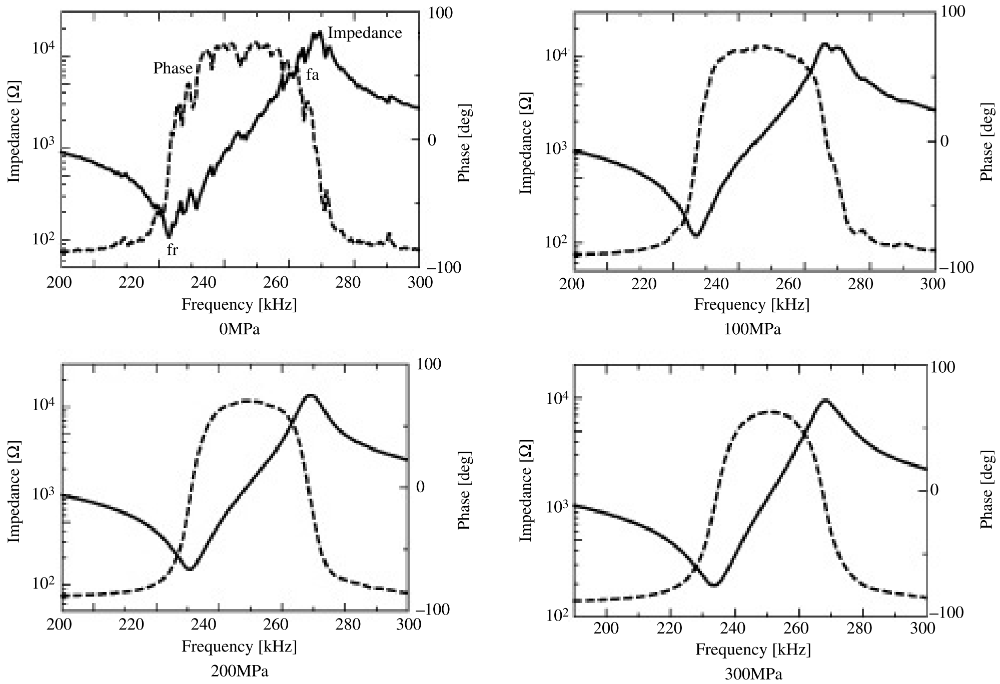


**Figure 2.** Resonance and antiresonance frequency characteristics of impedance and phase for the PMNT(68/32) single crystal oriented along the [001] axis in the $k_{31}$ mode for various pressures.

$f_r$ increased, while the antiresonance frequency $f_a$ remained almost constant (figure 3). The electromechanical coupling coefficient $k_{31}$ decreased, and the value of $k_{31}$ decreased by 16% at 400 MPa (figure 4). (3) The changes in the resonant impedance and the phase angle at $f_r$ and $f_a$ decreased. The mechanical quality factor $Q$ is the 3 dB width of the piezoelectric resonance divided into the resonance frequency [4, 12, 21]. A decrease in $Q$ with pressure was observed as shown in figure 5. The value of $Q$ for the $k_{31}$ mode is 72 at 25 °C in atmospheric pressure. These values were compared with the value of 35.3 for PMNT(65/35) [3] and 47 for PMNT(67/33) [6] single crystals in the thickness mode, and 41 for PZNT(91/9) in the $k_{31}$ mode [12] and 31.1 for PZNT(90.5/9.5) [3]. After the applied pressures were taken off, the resonance and antiresonance frequency characteristic curves were restored to those at 0 MPa.

### *3.2. Longitudinal electromechanical coupling properties*

The resonance and antiresonance frequency characteristics of the impedance and phase for the PMNT(68/32) single crystal oriented along the [001] axis in the $k_{33}$ mode in the rhombohedral phase were measured at 25 °C at atmospheric pressure and are shown in figure 6. The specimen had an electromechanical coupling coefficient of $k_{33}$ = 93.5% in the $k_{33}$ mode in the [001] poled single crystal bar. The piezoelectric constant $d_{33}$ was estimated to be 1797 pC $N^{-1}$ at atmospheric pressure. The relative permittivity $\varepsilon_r$ at 1 kHz was measured to be 5570 at 25 °C at atmospheric pressure. These values were compared with $k_{33} = 94\%$, $d_{33} = 2800$ pC $N^{-1}$ and $\varepsilon_r = 8200$ for PMNT(67/33) [7] and 92.3%, 1240 pC $N^{-1}$, $\varepsilon_r = 3100$ for PMNT(65/35) [3] and 80.8 [3] & 91.6% [23], 730 [3] & 1981 pC $N^{-1}$ [23] and 2890 [3] & 7800 [23] for PMNT(70/30), reported previously. The scattering seen in these values in the vicinity of

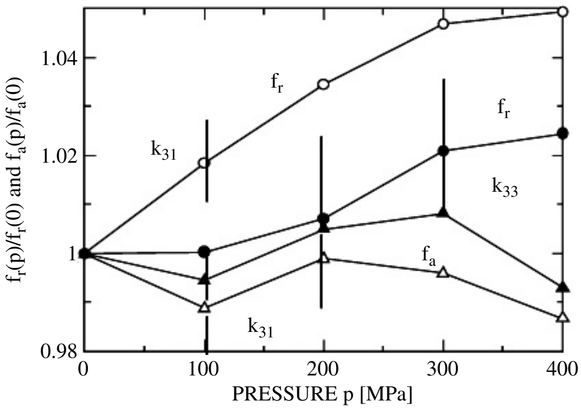


**Figure 3.** Changes in the resonance ($f_r$) and antiresonance ($f_a$) frequencies normalized with the $f_r$ and $f_a$ values at 0 MPa (denoted as $f_r/f_r(0)$ and $f_a/f_a(0)$, respectively) with pressure for the PMNT(68/32) single crystal oriented along the [001] axis in the $k_{31}$ (○, △) and $k_{33}$ (●, ▲) mode. The error indicated by vertical bars is due to the suspension system of the sample holder.

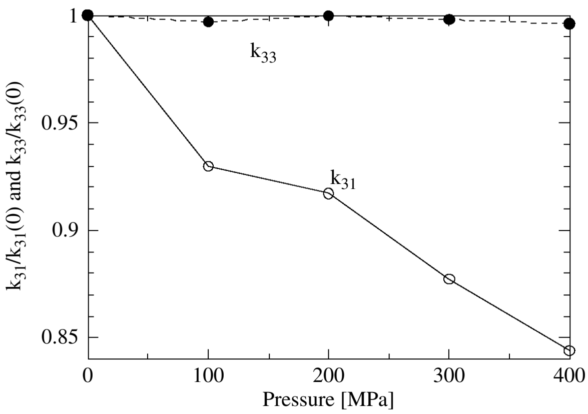


**Figure 4.** Changes in the electromechanical coupling factor $k_{31}$ (○) normalized with the $k_{31}$ value at 0 MPa (denoted as $k_{31}/k_{31}(0)$) and the $k_{33}$ (●) normalized with the $k_{33}$ value at 0 MPa (denoted as $k_{33}/k_{33}(0)$) with pressure for the PMNT(68/32) single crystal oriented along the [001] axis in the $k_{31}$ and $k_{33}$ modes at 25 °C.

the MPB composition may be due to the multi-domain structure created by poling a crystal along a nonpolar direction [10] and some $TiO_2$ distributions within [001] specimens [18]. Figure 7 shows the resonance and antiresonance frequency characteristics of the impedance and phase for the PMNT(68/32) single crystal oriented along the [001] axis in the $k_{33}$ mode in the rhombohedral phase for various pressures. The resonance frequency $f_r$ and the antiresonance frequency $f_a$ almost did not change with pressure in comparison with the case of the $k_{31}$ mode as also shown in figure 3. The electromechanical coupling coefficient $k_{33}$ remained almost constant with pressure as also shown in figure 4. Such a behaviour in the $k_{33}$ mode with pressure exhibited a marked contrast with the case of the $k_{31}$ mode with pressure mentioned above. The value of $Q$ was 103 at 25 °C at atmospheric pressure. This value was compared with the value of 112 for PMNT(67/33) in the beam mode [6] and 69 for PZNT(91/9) in the $k_{33}$ mode [12]. The change in $Q$ with pressure is also shown in figure 5. It is found in figure 5 that the value

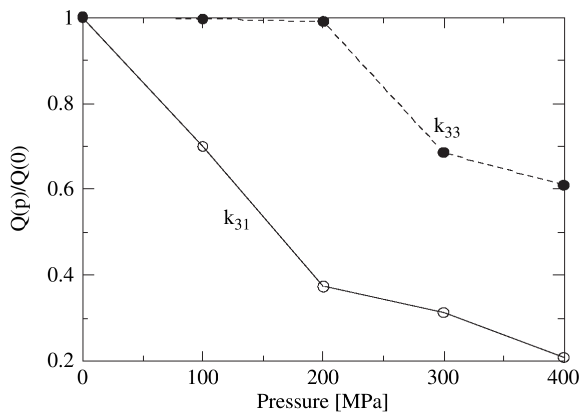


**Figure 5.** Changes in $Q$ normalized with $Q$ value at 0 MPa (denoted as $Q/Q(0)$) with pressures for a PMNT(68/32) single crystal along the [001] axis in $k_{31}$ (○) and $k_{33}$ (●) modes at 25 °C.

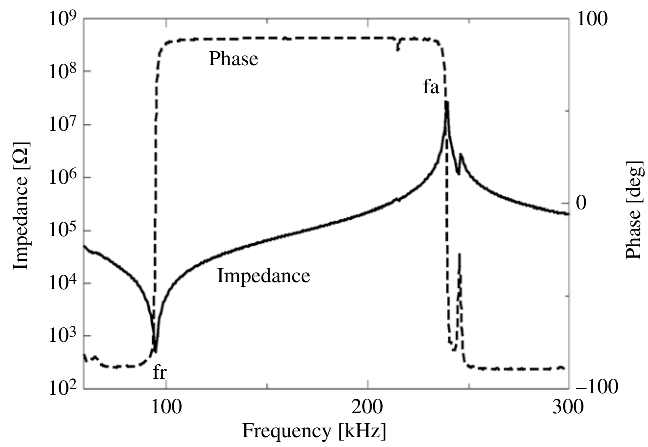


**Figure 6.** Resonance ($f_r$) and antiresonance ($f_a$) frequency characteristics of impedance and phase for the PMNT(68/32) single crystal oriented along the [001] axis in the $k_{33}$ mode at atmospheric pressure at 25 °C.

of $Q$ remained almost constant in the pressure range up to 200 MPa and then decreased with increasing pressure. After the applied pressures to the specimens were removed, the resonance and antiresonance frequency characteristic curves were recovered again.

## 4. Discussion

Since specimens along the [001] axis prepared from the single crystals grown by the Bridgman method were used for this experiment, there is some $TiO_2$ distribution within [001] specimens [18]. This may be one of the causes of scattering of the electromechanical coupling coefficient, the piezoelectric constant and the permittivity within the specimens [18]. After the electric field was taken off in the case of unipolar field versus strain characteristics of the rhombohedral single crystals along the [001] axis in the vicinity of the MPB compositions, the rhombohedral phase was restored for such electric-field-induced phase transformation [2].

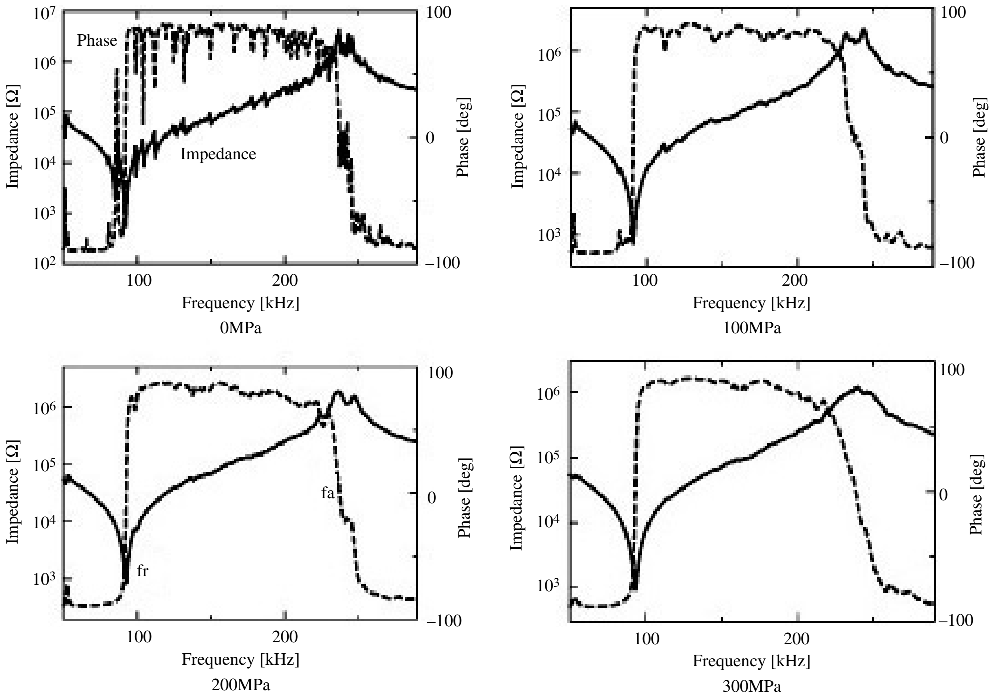


**Figure 7.** Resonance and antiresonance frequency characteristics of impedance and phase for the PMNT(68/32) single crystal oriented along the [001] axis in the $k_{33}$ mode for various pressures.

Thus the rhombohedral phase was considered to be restored after the poling field was removed. Consequently, the large $k_{33}$ and $k_{31}$ values appearing on these [001] specimens were found in this work (see section 3). The hydrostatic piezoelectric coefficient $d_h$ was estimated to be 151 pC $N^{-1}$ with the relationship of $d_h = 2d_{31} + d_{33}$ [19]. This value was compared with $d_h = 108$ pC $N^{-1}$ for PMNT(70/30) along the [001] axis with domain-engineered structure reported previously by the hydrostatic piezoelectric coefficient measurement [19].

The relationship between the resonant frequency $f_r$ or the antiresonant frequency $f_a$ and the elastic compliance $s^E$ for the constant field $E$ or $s^D$ for constant charge density $D$ is given by the following equation [21]:

$$2f_r l = 1/(gs^E)^{0.5}; \qquad 2f_a l = 1/(gs^D)^{0.5}, \tag{1}$$

where $s^E$ is $s_{11}^E$ for the transverse $k_{31}$ mode or $s_{33}^D$ for the longitudinal $k_{33}$ mode, $g$ the density and $l$ the dimension of the specimen in the direction of the transverse or longitudinal wavevector. The elastic compliance $s_{33}^E$ is given by the relation $s_{33}^E = s_{33}^D/(1 - k_{33}^2)$. The values of the elastic compliances $s_{11}^E$ and $s_{33}^E$ at 25 °C at atmospheric pressure were estimated to be 39.0 and 78.9 × $10^{-12}$ $m^2$ $N^{-1}$, respectively, using $g = 8.06$ g $cm^{-3}$ [7] with equation (1). These values of $s_{11}^E$ and $s_{33}^E$ were respectively compared with 69.0 and 119.6 × $10^{-12}$ $m^2$ $N^{-1}$ for PMNT(67/33) reported [7] previously. If the value of $g$, 8.06 g $cm^{-3}$, is assumed to be almost constant in the pressure range up to 400 MPa, the pressure dependence of the elastic compliances $s_{11}^E$ and $s_{33}^E$ in the PMNT(68/32) single crystal is as shown in figure 8. As the applied pressure increased, $s_{11}^E$ or $s_{33}^E$ decreased and the mechanical hardness in the PMNT(68/32) single crystal increased with pressure in the rhombohedral phase. The values of $s_{11}^E$ and $s_{33}^E$ at 400 MPa were estimated to be 35.4 and 75.1 × $10^{-12}$ $m^2$ $N^{-1}$, respectively. The

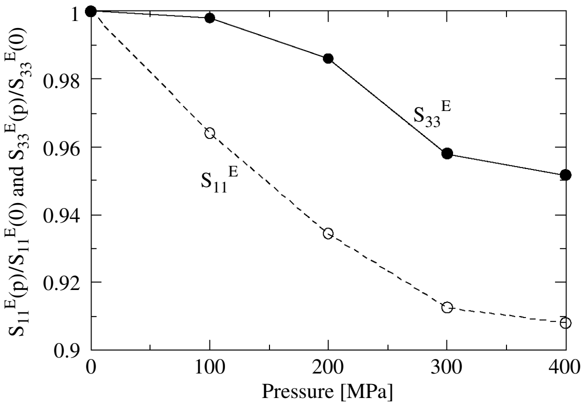


**Figure 8.** Changes in the elastic compliances $s_{11}^E$ (○) and $s_{33}^E$ (●) normalized with the $s_{11}^E$ and $s_{33}^E$ values at 0 MPa (denoted as $s_{11}^E/s_{11}^E(0)$ and $s_{33}^E/s_{33}^E(0)$, respectively) with pressure for the PMNT(68/32) single crystal poled along the [001] axis in the rhombohedral phase in the $k_{31}$ and $k_{33}$ modes at 25 °C.

**Table 1.** Values of $s_{11}^E$, $s_{33}^E$, $k_{31}$ and $k_{33}$ poled along the [001] axis in the rhombohedral phase in the PMNT(68/32) single crystal.

| PMNT | 0 MPa | 400 MPa |
|---|---|---|
| $s_{11}^E (10^{-12}\ \mathrm{m^2\ N^{-1}})$ | 39 | 35.4 |
| $s_{33}^E (10^{-12}\ \mathrm{m^2\ N^{-1}})$ | 78.9 | 75.1 |
| $k_{31}$ (%) | 62.8 | 53 |
| $k_{33}$ (%) | 93.5 | 93 |

values of $s_{11}^E$, $s_{33}^E$, $k_{31}$ and $k_{33}$ are summarized in table 1. It has been known [2, 4–12] that the superior piezoelectricity along the [001] axis in the rhombohedral phase for single crystals is based on the domain stability due to the engineered domain configuration. From the viewpoint of the engineered domain concept [2, 4–12] it is thought that the stable domain configuration consisting of four polarization pairs poled along the [001] axis in the rhombohedral phase is responsible for the longitudinal wave in the $k_{33}$ mode, while the unstable domain configuration consisting of only two polarization pairs poled along the [001] axis in the rhombohedral phase is responsible for the transverse wave in the $k_{31}$ mode. By applying external loads such as pressures to the specimens, the remarkable contrast between the $k_{33}$ value almost constant with $p$ and the $k_{31}$ value with a large decrease with $p$ seems to appear [11, 12]. Furthermore, the existence of mobile domain walls has been known to reduce $Q$ [4, 21]. The contrast between the $Q$ value in the $k_{33}$ mode almost constant with $p$ and the $Q$ value in the $k_{31}$ mode with the large decrease with $p$ in the pressure range up to 200 MPa also seems to be due to the existence of more mobile domain walls in the $k_{31}$ mode than in the $k_{33}$ mode [12, 21]. On the other hand, superior piezoelectric properties were recently reported to come from the large shear mode of $d_{15}$ [9, 10]. The large shear mode in the piezoelectric properties cannot be influenced by the hydrostatic pressure, since uniform pressure introduces no shearing stresses [24]. Thus for $k_{33}$ and $k_{31}$ modes the lack of change in $k_{33}$ and $k_{31}$ values with $p$ is considered from the viewpoint of the contribution of the large shear mode [9]. However, from the viewpoint of the contribution of the multi-domain state [10] through the existence of mobile domain walls as mentioned above, the decrease in $k_{31}$ and $Q$ values with $p$ for the $k_{31}$ mode is considered.

## 5. Conclusions

Hydrostatic pressures up to 400 MPa were applied to the PMNT(68/32) single crystal plate poled along the [001] axis for the $k_{31}$ mode and the bar for the $k_{33}$ mode. With increasing hydrostatic pressure ($p$), the resonance frequency $f_r$ increased for the $k_{31}$ mode, while the antiresonance frequency $f_a$ remained almost constant. The electromechanical coupling coefficient $k_{31}$ decreased markedly, and the $k_{31}$ value decreased by 16% at 400 MPa. Such a decrease in the $k_{31}$ mode with $p$ is due to both the decrease in the difference $\Delta f$ between $f_r$ and $f_a$ and the increase in $f_r$ with $p$. On the other hand, the electromechanical coupling coefficient $k_{33}$ remained almost constant with $p$. The large decrease in the $k_{31}$ value with $p$ exhibited a marked contrast with the $k_{33}$ value almost constant with $p$. The changes in the values of the elastic compliances $s_{11}^E$ and $s_{33}^E$ with $p$ were found to be large from the changes in the resonant and antiresonant frequencies with $p$. $s_{11}^E$ and $s_{33}^E$ at 400 MPa were estimated to be 35.4 and $75.1 \times 10^{-12}$ m$^2$ N$^{-1}$, respectively. The values of $k_{31}$ in the $k_{31}$ mode and $k_{33}$ in the $k_{33}$ mode at 400 MPa were estimated to be 53 and 93%, respectively. These values of PMNT(68/32) were compared with $s_{11}^E = 72.3 \times 10^{-12}$ m$^2$ N$^{-1}$, $s_{33}^E = 139.5 \times 10^{-12}$ m$^2$ N$^{-1}$, $k_{31} = 68.6\%$, and $k_{33} = 89.8\%$ of PZNT(91/9) at 400 MPa [11]. PMNT(68/32) single crystals are mechanically harder than PZNT(91/9) ones. Superior piezoelectric properties in the rhombohedral [001] single crystal with the multi-domain state in the vicinity of the MPB composition were recently pointed out [9, 10] to come from the contribution of the large shear piezoelectric constant $d_{15}$ of the rhombohedral single crystal with the single domain property. Since the hydrostatic pressure introduces no shearing stresses, uniform pressure cannot influence the piezoelectric properties from the viewpoint of the contribution of the large shear mode of $d_{15}$. On the other hand, from the engineered domain concept, the $k_{33}$ value in the $k_{33}$ mode almost constant with $p$ is considered to be due to the stable domain configuration responsible for the longitudinal $k_{33}$ mode. Consequently, the large $k_{33}$ PMNT(68/32) rhombohedral single crystal poled along the [001] direction is considered to be useful for the application of ultrasonic devices under water.

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