

Pressure-modulated free energy change in piezoelectric and dielectric responses for relaxor ferroelectric solid solution $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ binary system single crystal and ceramics near a morphotropic phase boundary composition

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(Received 11 December 2007; accepted 13 January 2008; published online 20 March 2008)

The electromechanical and dielectric responses in transverse and longitudinal modes for relaxor ferroelectric solid solution $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMNT) near a morphotropic phase boundary composition were investigated under hydrostatic pressures up to 700 MPa at 25 °C. The effect of pressure on their responses remarkably appeared. Their electromechanical suppression in PMNT single crystal and ceramics occurs at each pressure, corresponding to electromechanical coupling coefficient k . The permittivity ϵ increased with pressure-induced electromechanical suppression. The change in ϵ with such suppression corresponds to k . Such phenomena were considered to be due to the increase in piezoelectric load based on decrease of domain size coming from increase in free energy with pressures. © 2008 American Institute of Physics.
[DOI: 10.1063/1.2896586]

I. INTRODUCTION

Relaxor based ferroelectric solid solution $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMNT) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZNT) binary system single crystal and ceramics near a morphotropic phase boundary (MPB) are of particular interests and in future useful for applications in ultrasonic, nondestructive testing, and actuator devices, making use of superior electromechanical properties.¹⁻⁴ Such piezoelectric properties for their solid solutions near a MPB composition has been reported⁵⁻⁹ to come from large shear modulus d_{15} of the single domain state. They were concerned with the intrinsic crystal lattice deformation effect⁵⁻⁸ and the extrinsic one^{5,6,9} related to the engineered domain configuration in which the domain wall structure is stabilized by the oblique poling field. The pressure effect of piezoelectric properties of $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$ [abbreviated PZNT (91/9)] binary system single crystal was previously dealt with¹⁰ from the viewpoint of large shear modulus d_{15} . Samara *et al.*¹¹ reported the strong effect of pressure on free energy through

dielectric responses in PZNT binary system. On the other hand, it was pointed out^{12,13} that the relation between the crystallographic symmetry and the ability of a ferroelectric polycrystalline ceramic to switch is important. For the piezoelectric activity,^{4,13} domains in ferroelectric ceramics must be polarized and distorted by poling process which causes some of the domains to switch so that the polarization will be aligned along the poling direction. Free energy minimizing domain configuration provides enhanced electromechanical property.^{13,14} BaTiO_3 ceramics with larger piezoelectric constant of 350 pC/N, planar electromechanical coupling coefficient of 35%, and small grain sizes of a few micrometers were recently fabricated by microwave sintering process making use of controlling changes in microstructures.¹⁵ On the other hand, ferroelectric systems with very low domain wall energies have been shown¹⁶ from the martensite phase transformation theory to form miniaturized microdomain structures which minimize the transformation stress. In this work, the pressure effect of piezoelectric properties in PMNT binary system single crystal and ceramics near a MPB composition are dealt with from the viewpoint of pressure-modulated free energy change in piezoelectric and

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dielectric responses. The piezoelectric and dielectric properties of $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.68}\text{Ti}_{0.32}\text{O}_3]$ [abbreviated PMNT(68/32)] binary system single crystal poled along the [001] direction in the rhombohedral phase, PMNT(67/33) ceramic poled in the tetragonal phase, and PMNT(76/24) ceramic poled in the rhombohedral one were investigated under pressure (p) up to 700 MPa at 25 °C. The remarkable effects of hydrostatic pressures on them were presented and their properties were discussed from the viewpoint of the change in domain size due to the pressure-modulated free energy change. The change in relative permittivity with pressure-induced suppression of electromechanical response, correspondingly to electromechanical coupling coefficient k , was presented in this paper.

II. EXPERIMENTAL PROCEDURE AND SAMPLE PREPARATION

PMNT(68/32) single crystals were obtained by a conventional solution Bridgman method.^{17,18} The detailed specimen preparation was described elsewhere.¹⁹ The single crystal plate with dimensions of $4.00(\text{w}) \times 1.23(\text{l}) \times 0.33(\text{t}) \text{ mm}^3$ for the measurement of the k_{31} (d_{31}) mode and the single crystal bar with dimensions of $2.50(\text{w}) \times 2.50(\text{l}) \times 7.50(\text{t}) \text{ mm}^3$ for the measurement of the k_{33} (d_{33}) mode were prepared from a (001) crystal. PMNT(67/33) and (76/24) ceramics were prepared using the columbite precursor method.^{20,21} The rectangular plate specimen with dimensions of $3.1(\text{w}) \times 12.9(\text{l}) \times 1.0(\text{t}) \text{ mm}^3$ for PMNT(67/33) and $3.1(\text{w}) \times 13.3(\text{l}) \times 1.0(\text{t}) \text{ mm}^3$ for PMNT(76/24) were prepared for the measurement of the k_{31} mode. The disk specimen with dimensions of $16.0 \text{ mm } \varphi$ and 1.0 mm thickness was prepared for the measurement of the planar coupling coefficient k_p . 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 electric field at 40 °C for 15 min for single crystal and in a 15 kV/cm electric field while cooling from well above the transition to 25 °C for ceramic in an insulating liquid, silicone oil, to prevent arc. The electromechanical coupling factors k were measured by the resonance and antiresonance frequency methods using an impedance gain phase analyzer (HP-4194A; network mode).⁴ The pressure apparatus used to apply hydrostatic pressures to specimens was described elsewhere.^{10,22} The piezoelectric constant d was measured using a strain meter (Millitron No. 1240).

III. RESULTS

A. Piezoelectric response

1. PMNT(68/32) single crystal

The rhombohedral PMNT(68/32) single crystal specimen had an electromechanical coupling coefficient $k_{31} = 62.8\%$ for the k_{31} mode, the piezoelectric constant $d_{31} = -830 \text{ pC/N}$, $\epsilon_r = 5000$, and $\tan \delta = 0.0014$ at 1 kHz in the [001] poled single crystal plate in atmospheric pressure. These values are comparable to $k_{31} = 59\%$, $d_{31} = -1330 \text{ pC/N}$, $\epsilon_r = 4233$, and $\tan \delta = 0.009$ (Ref. 23) of

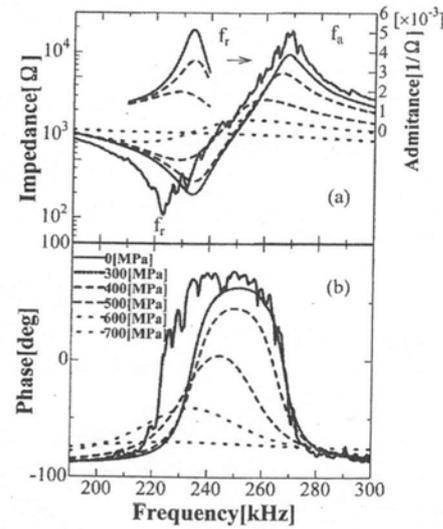


FIG. 1. Resonance and antiresonance frequency characteristics of (a) impedance and admittance in the vicinity of f_r and (b) phase for the PMNT(68/32) rhombohedral single crystal poled along the [001] axis in the k_{31} mode for various pressures.

PMNT(67/37) reported previously. Figure 1(a) shows the impedance frequency characteristic curves for the k_{31} mode for increasing pressures (p). Electrical reflections from the pressure chamber walls were found to be reduced due to the decrease in electrical sensitivity of the specimen element with increasing p .²⁴ Its curve became broader with increasing p up to 400 MPa. The resonance and antiresonance behaviors were strongly suppressed at pressures above 500 MPa. Figure 1(b) shows the phase changes with p . The distinct phase change at f_r and f_a were observed below 400 MPa. These changes were abruptly disappeared above 500 MPa. The piezoelectric response became weaker ($k_{31} = 53\%$ at 400 MPa) (Ref. 19) due to the increase of f_r and the decrease of difference Δf between f_r and f_a with p and finally disappeared. The increase in asymmetry in shape with p seen in the admittance curves in the vicinity of f_r as also shown in Fig. 1(a), suggests the enhanced electrostrictive component with p . Such behavior was previously observed in the case of elastically hardening for PMNT(90/10).²⁵ For the longitudinal k_{33} mode, its specimen had $k_{33} = 93.5\%$, $d_{33} = 1790 \text{ pC/N}$, and $\epsilon_r = 4887$ at 1 kHz at 25 °C at atmospheric pressure. These values are comparable to $k_{33} = 94\%$, $d_{33} = 2800 \text{ pC/N}$, and $\epsilon_r = 8200$ of PMNT(67/33).⁵ Figures 2(a) and 2(b) show their frequency characteristic curves for the longitudinal k_{33} mode for various pressures (p). Their frequency characteristics remain almost constant to about 500 MPa. At pressures above 500 MPa, they became broader with increasing p . Meanwhile piezoelectric response became weaker. The admittance curves in the vicinity of f_r are also shown in Fig. 2(a) and the symmetry in shape under various pressures was observed in contrast to the case of k_{31} mode. Such behavior suggests the strong piezoelectricity of the specimen.

2. PMNT(67/33) and PMNT(76/24) ceramics

The tetragonal PMNT(67/33) ceramic specimen had $k_p = 51\%$ in the k_p mode, $k_{31} = 28.4\%$, $d_{33} = 440 \text{ pC/N}$, ϵ_r

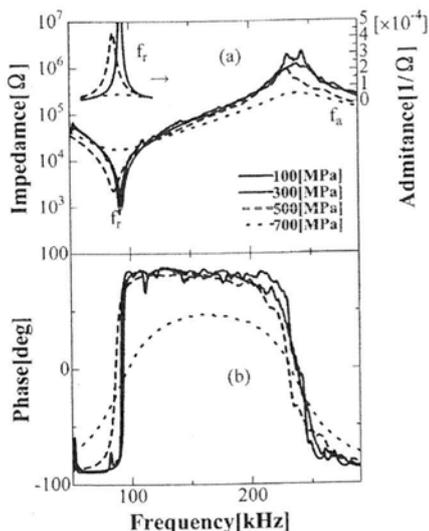


FIG. 2. Resonance and antiresonance frequency characteristics of (a) impedance and admittance in the vicinity of f_r and (b) phase for the PMNT(68/32) rhombohedral single crystal poled along the [001] axis in the k_{33} mode for various pressures.

$=2752$, and $\tan \delta=0.023$ at 1 kHz at 25 °C at atmospheric pressure. These values are compared with $k_p=18.2\%$ for PMNT(62.5/37.5),²⁶ $d_{33}=456$ pC/N, $\epsilon_r=3119$, and $\tan \delta=0.006$ for PMNT(65/35).²¹ Figures 3(a) and 3(b) show their frequency characteristic curves for the k_{31} mode for various pressures. The effect of pressure on those for the k_{31} mode was found to be striking. The suppression occurs at pressures above 490 MPa and the piezoelectric response finally disappeared. The rhombohedral PMNT(76/24) ceramic specimen had $k_p=36.4\%$, $k_{31}=21.5\%$, $d_{33}=245$ pC/N, $\epsilon_r=2188$, and $\tan \delta=0.028$ at 1 kHz at 25 °C at atmospheric pressure. These values are compared with $k_p=14.4\%$ for PMNT(75/25).²⁶ $d_{33}=305$ pC/N, $\epsilon_r=2435$, and $\tan \delta=0.018$ for PMNT(75/25).²¹ Figures 4(a) and 4(b) show their frequency characteristic curves for the k_{31} mode for

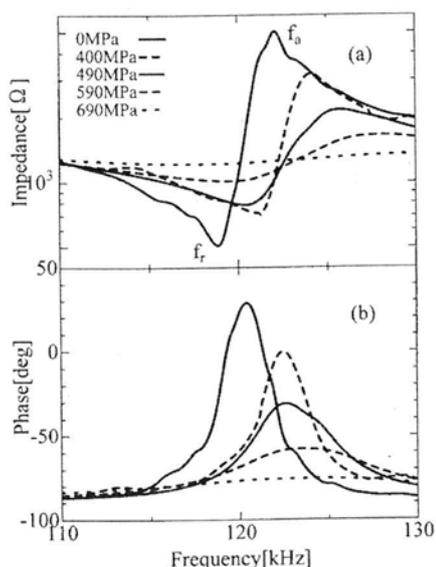


FIG. 3. Resonance and antiresonance frequency characteristics of (a) impedance and (b) phase for the poled PMNT(67/33) tetragonal ceramic in the k_{31} mode for various pressures.

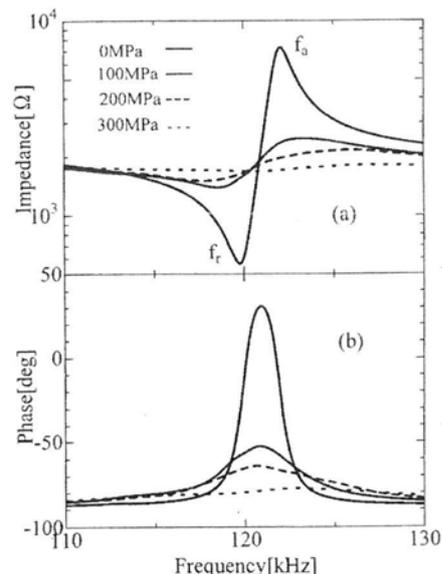


FIG. 4. Resonance and antiresonance frequency characteristics of (a) impedance and (b) phase for the poled PMNT(76/24) rhombohedral ceramic in the k_{31} mode for various pressures.

various pressures. The effect of pressure on those for the k_{31} mode was very striking. The suppression occurs at pressures above 100 MPa and the piezoelectric response finally disappeared at 300 MPa. After the applied pressures to the specimens were taken off in each case, the resonance and antiresonance characteristic curves were restored to those at 0 MPa.

B. Dielectric response

Figure 5 shows the change in the relative permittivity ϵ_r for various electromechanical responses with applied pressures. The ϵ_r increases with p in each case. The magnitude of the change $\Delta\epsilon_r$ in ϵ_r with such pressure-induced suppression of electromechanical response was found from Fig. 5 to be $\Delta\epsilon_r > 5517$ for k_{33} mode and 2002 for k_{31} in the rhombohedral PMNT(68/32) single crystal and 503 for k_{31} mode in the PMNT(67/33) tetragonal ceramic and 113 for k_{31} in the PMNT(76/24) rhombohedral ceramic, respectively. On the other hand, values of their electromechanical coupling coefficients k were $k_{33}=94.0$ and $k_{31}=61.5\%$ for rhombohedral PMNT(68/32) single crystal and $k_{31}=28.5\%$ for PMNT(67/33) tetragonal ceramic and $k_{31}=21.5\%$ for

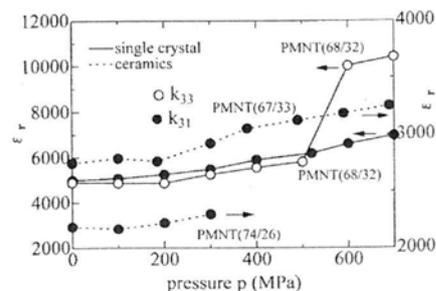


FIG. 5. Pressure dependences of relative permittivity ϵ_r for PMNT binary system single crystal and ceramics near a MPB composition at 1 kHz at 25 °C.

PMNT(76/24) rhombohedral ceramic, respectively. Thus the magnitude of $\Delta\epsilon_r$ seems to correspond to that of k .

IV. DISCUSSION

Such pressure-induced suppression of electromechanical responses are explained as follows. Ferroelectric domain configurations which are energetically favored are formed under electromechanical load with poling process, leading to macroscopic piezoelectricity.¹⁴ The domains need to be arranged electromechanically to minimize their interaction energy, leading to complicated domain configurations with the size of domains regulated by the domain wall energy.¹⁴ According to the martensite theory¹⁶ developed thermodynamically and crystallographically, the typical domain size λ is given by the following relation:

$$\lambda = \beta[\gamma D / \mu \epsilon_0^2]^{1/2},$$

where β is the dimensionless constant, D the thickness of the polydomain plate, γ the domain wall energy, μ the shear modulus, and ϵ_0 the twinning strain. When pressures are applied to specimen, the free energy of specimen is increased.^{11,27} This increase in free energy with p leads to a reduction of domain wall energy to reduce such increase in free energy.^{11,27} The domain size is found from above relation through the decrease in γ to decrease.^{11,16} Wada *et al.*²⁸ have reported that the decrease in domain size leads to the increase in piezoelectric load with both the increase in ϵ_r and the increase in elastic compliance. The increase in $\Delta\epsilon_r$ with pressure-induced suppression of electromechanical response and its magnitude corresponding to the electromechanical coupling coefficient k (as described in Sec. III B) suggest the decrease in domain size with p . Consequently, pressure-induced suppression of electromechanical responses with the increase in ϵ_r with p appears. In the rhombohedral plate poled along the [001] axis, the resultant polarization, direction is [001] axis in the case of domain configuration consisting of 71° and 109° domains.^{19,29} Piezoelectric constants d_{33}^* and d_{31}^* along the <001> direction in the rhombohedral phase are given 1.10 by the following relations:

$$d_{33}^* = (2\sqrt{2}d_{22} + 2d_{31} + d_{33} + 2d_{15})/3\sqrt{3}$$

and

$$d_{31}^* = (-\sqrt{2}d_{22} + 2d_{31} + d_{33} - d_{15})/3\sqrt{3},$$

respectively, where d_{22} , d_{31} , d_{33} , and d_{15} are fundamental piezoelectric components of the single domain state in $3m$ symmetry. The values of d_{15} , d_{22} , d_{31} , and d_{33} were 4100 pC/N, 1340 pC/N, -90 pC/N, and 190 pC/N, respectively, for the PMNT(67/33) single domain single crystal.⁶ The origin of the large piezoelectric properties was reported^{6,9,10} to come from such large shear mode d_{15} . The values of d_{33}^* and d_{31}^* are estimated from above relations to be 2305 pC/N and -1150 pC/N, respectively. Subsequently, the piezoelectric constant d_{33}^* responsible for the longitudinal wave in k_{33} mode is larger than d_{31}^* responsible for the transverse wave in k_{31} mode. Thus the pressure at which electromechanical response depresses is larger in k_{33} than k_{31} mode.

On the other hand, for ferroelectric ceramics, according to the theory due to the free energy minimizing domain configuration, the domain switching is difficult to occur in the tetragonal phase, and the remanent polarization is a third of spontaneous polarization,¹³ whereas the domain switching is easy to occur in the rhombohedral phase near a MPB composition and the remanent polarization is about equal to the spontaneous polarization.¹³ Therefore, once domain configurations laminated with poling are formed in these specimens, its domain configuration is more stable for the transverse k_{31} mode in the tetragonal phase than in the rhombohedral one. Thus the pressure at which such suppression appears is larger in the tetragonal phase than in the rhombohedral one.

V. SUMMARY

The pressure-induced suppression of electromechanical response for each mode in PMNT single crystal and ceramics occurs at each pressure. The ϵ_r for each mode increases with pressure-induced electromechanical suppression. The magnitude of such increase in ϵ_r corresponds to that of electromechanical coupling coefficient k . The increase in $\Delta\epsilon_r$ with pressure-induced suppression of electromechanical response is considered to be based on decrease in domain size due to the increase in free energy with applied pressure. The large k_{33} PMNT(68/32) rhombohedral single crystal poled along the [001] direction and the large k_{31} PMNT tetragonal poled ceramics with small grain sizes near a MPB composition are considered to be useful for the application of ultrasonic device under water.

ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research (B) (No. 16360150) from the Japan Society for the Promotion of Science.

- ¹J. Kuwata, K. Uchino, and S. Nomura, *Jpn. J. Appl. Phys., Part 1* **21**, 1298 (1982).
- ²S. E. Park and T. R. Shrout, *Mater. Res. Innovations* **1**, 20 (1997).
- ³T. Kobayashi, S. Shimanuki, S. Saitoh, and Y. Yamashita, *Jpn. J. Appl. Phys., Part 1* **36**, 6035 (1997).
- ⁴N. Setter, *Piezoelectric Materials in Devices* (Ceramics Laboratory EPFL Swiss Federal Institute of Technology, Lausanne, 2002) Chap. 1.
- ⁵R. Zhang, B. Jiang, and W. Cao, *J. Appl. Phys.* **90**, 3471 (2001).
- ⁶R. Zhang, B. Jiang, and W. Cao, *Appl. Phys. Lett.* **82**, 787 (2003).
- ⁷D. Damjanovic, M. Budimir, M. Davis, and N. Setter, *Appl. Phys. Lett.* **83**, 527 (2003).
- ⁸J. Han and W. Cao, *Appl. Phys. Lett.* **83**, 2040 (2003).
- ⁹M. Davis, D. Damjanovic, D. Hayem, and N. Setter, *J. Appl. Phys.* **98**, 014102 (2005).
- ¹⁰N. Yasuda, Md. M. Rahman, H. Ohwa, M. Matsushita, Y. Yohachi, M. Iwata, H. Terauchi, and Y. Ishibashi, *Appl. Phys. Lett.* **89**, 192903 (2006).
- ¹¹G. A. Samara, E. L. Venturini, and V. H. Schmidt, *Appl. Phys. Lett.* **76**, 1327 (2000).
- ¹²W. Cao, *Nat. Mater.* **4**, 727 (2005).
- ¹³J. Y. Li, R. C. Rogan, E. Ustundag, and K. Bhattacharya, *Nat. Mater.* **4**, 776 (2005).
- ¹⁴J. Yu Li and D. Liu, *J. Mech. Phys. Solids* **52**, 1719 (2004).
- ¹⁵H. Takahashi, Y. Numamoto, J. Tani, and S. Tsurekawa, *Jpn. J. Appl. Phys., Part 1* **45**, 7405 (2006).
- ¹⁶Y. M. Jin, Y. U. Wang, A. G. Khachatryan, J. F. Li, and D. Viehland, *J. Appl. Phys.* **94**, 3629 (2003).
- ¹⁷M. Matsushita, Y. Tachi, and K. Echizenya, Abstract American Ceramic Society, 103rd Annual Meeting, 2001, p. 247.
- ¹⁸Y. Yamashita, Y. Hosono, K. Harada, and Z.-G. Ye, *Piezoelectric Materi-*

- als in Devices* (Ceramics Laboratory EPFL Swiss Federal Institute of Technology, Lausanne, 2002), p. 455.
- ¹⁹N. Yasuda, T. Banno, K. Fujita, H. Ohwa, M. Matsushita, Y. Yamashita, M. Iwata, and Y. Ishibashi, *J. Phys.: Condens. Matter* **18**, 7659 (2006).
- ²⁰S. L. Swartz and T. R. Shrout, *Mater. Res. Bull.* **17**, 1245 (1982).
- ²¹S. W. Choi, T. R. Shrout, S. J. Jang, and A. S. Bhalla, *Ferroelectrics* **100**, 29 (1989).
- ²²N. Yasuda, M. Okamoto, H. Shimizu, and S. Fujimoto, *Phys. Rev. B* **20**, 2755 (1979).
- ²³H. Luo, G. Xu, H. Xu, P. Wang, and Z. Yin, *Jpn. J. Appl. Phys., Part 1* **39**, 5581 (2000).
- ²⁴R. V. Wilhelm and M. G. McLaren, *Ceram. Bull.* **54**, 714 (1975).
- ²⁵D. Viehland, S. J. Jang, E. Cross, and M. Wuttig, *Philos. Mag. A* **64**, 835 (1991).
- ²⁶H. Ouchi, K. Nagano, and S. Hayakawa, *J. Am. Ceram. Soc.* **48**, 630 (1965).
- ²⁷R. Y. Nishi and R. F. Brown, *J. Acoust. Soc. Am.* **36**, 1292 (1964).
- ²⁸S. Wada, K. Yako, H. Kakemoto, T. Tsurumi, and T. Kiguchi, *J. Appl. Phys.* **98**, 014109 (2005).
- ²⁹N. Yasuda, Y. Itoh, H. Ohwa, M. Matsushita, Y. Yamashita, M. Iwata, and Y. Ishibashi, *J. Korean Phys. Soc.* **46**, 124 (2005).