

Dielectric/piezoelectric resonance in high-strain $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ crystals

Chi-Shun Tu, R. R. Chien, V. H. Schmidt, F.-T. Wang, W.-T. Hsu, C.-T. Tseng, and C. C. Shih

Citation: *Journal of Applied Physics* **97**, 126105 (2005); doi: 10.1063/1.1948523

View online: <http://dx.doi.org/10.1063/1.1948523>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/97/12?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

Effect of crystal orientation on the phase diagrams, dielectric and piezoelectric properties of epitaxial BaTiO_3 thin films

AIP Advances **6**, 015309 (2016); 10.1063/1.4940205

Poling effect and piezoelectric response in high-strain ferroelectric $0.70\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.30\text{PbTiO}_3$ crystal

J. Appl. Phys. **108**, 044101 (2010); 10.1063/1.3475150

Phase diagrams, dielectric response, and piezoelectric properties of epitaxial ultrathin (001) lead zirconate titanate films under anisotropic misfit strains

J. Appl. Phys. **107**, 114105 (2010); 10.1063/1.3386465

Electric-field-induced dielectric anomalies and optical birefringence in $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.10$) single crystal

J. Appl. Phys. **100**, 074105 (2006); 10.1063/1.2356905

Growth and characterization of Fe-doped $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - \text{PbTiO}_3$ single crystals

J. Appl. Phys. **93**, 9257 (2003); 10.1063/1.1571966



NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP | Applied Physics Reviews

Dielectric/piezoelectric resonance in high-strain $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ crystals

Chi-Shun Tu

Graduate Institute of Applied Science and Engineering, Fu Jen University, Taipei 242, Taiwan, Republic of China

R. R. Chien^{a)} and V. H. Schmidt

Department of Physics, Montana State University, Bozeman, Montana 59717

F.-T. Wang, W.-T. Hsu, C.-T. Tseng, and C. C. Shih

Department of Physics, Fu Jen University, Taipei 242, Taiwan, Republic of China

(Received 28 April 2005; accepted 18 May 2005; published online 24 June 2005)

This work presents dielectric resonance in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ crystals after electric (E)-field poling, which is crucial for piezoelectric applications. Dielectric permittivity has been measured as functions of temperature, frequency, poling E -field strength, and Ti content ($x=25\%$ and 34%). Frequency-dependent dielectric spectroscopy after poling exhibits multiple piezoelectric resonances between 0.2 and 1 MHz, and can be described by the forced-damped-oscillator model. The resonant spectra show significant changes while phase transitions are taking place. © 2005 American Institute of Physics. [DOI: 10.1063/1.1948523]

High-strain ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PMNT) crystals have demonstrated piezoelectric effects much larger than conventional $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) ceramics.¹ Physical properties of PMNT strongly depend on Ti content, poling electric (E)-field strength, and crystallographic orientation.^{2–4} It was found that the monoclinic (M) phase plays an essential role in bridging higher symmetries [rhombohedral (R), tetragonal (T), and cubic (C)] while phase transitions are taking place.⁴ Though these crystals have been studied extensively in recent years, there are still many application issues and unclear physical origins to be addressed. To enhance piezoelectric performance, an E -field poling has usually been used on these materials before application. However, how an E -field poling affects dielectric spectroscopy still remains unclear, particularly for an operating frequency above 100 kHz.

Piezoelectric resonances have been observed in poled PZT ceramics⁵ and piezoelectric polymers.⁶ A field-induced piezoelectric resonance was seen in paraelectric $\text{BaTi}_{0.8}\text{Sn}_{0.2}\text{O}_3$ ceramic, which vanished after removing the bias field.⁷ These dielectric resonances were found to be associated with vibrations of microscopic ionic units and various extension modes. A detailed theoretical review of piezoelectric resonance for polymers can be found in Ref. 6.

In this study, the PMNT crystals were cut perpendicular to the $\langle 111 \rangle$ direction. Hereafter, $x\%$ stands for (111) -oriented $\text{PMNT}_x\%$. The Ti concentration ($x\%$) was determined by using the dielectric maximum temperature T_m upon heating.⁴ A Wayne–Kerr precision analyzer PMA3260A with four-lead connections was used to obtain real ϵ' and imaginary ϵ'' parts of dielectric permittivity. A Janis CCS-450 cold head was used with a Lakeshore 340 temperature controller. Gold electrodes were deposited on sample surfaces by sputtering.

The sample thicknesses are 1.0 and 0.6 mm for 25% and 34%, respectively. Two processes were used in the dielectric measurements. The first is called “zero-field heating” (ZFH), in which the data were taken upon heating without any E -field poling. In the second process, FR-ZFH, the sample was poled at room temperature (RT) along $[111]$ with a dc E field for about 1 h before ZFH was performed. The hysteresis loop of electric field versus polarization was also measured by using a Sawyer–Tower circuit at $f=46$ Hz.

Figures 1(a) and 1(b) show the temperature-dependent ϵ' and ϵ'' at several frequencies obtained from ZFH and FR-ZFH for 25% and 34%, respectively. For measuring frequencies below 100 kHz, besides a broad maximum at $T_m \cong 390$ K, 25% shows an extra peak near 368 K in ϵ' (FR-ZFH). For 34%, instead of a gradual anomaly near 325 K in ϵ' (ZFH), a step-up anomaly is seen near 340 K in ϵ' (FR-ZFH) below 100 kHz. The dielectric maximum temperatures (T_m) of ϵ' (ZFH) and ϵ' (FR-ZFH) in 34% are, respectively, 434 and ~ 438 K, where the tetragonal-cubic ferroelectric transition occurs. Dielectric spectra of ϵ' (FR-ZFH) above 100 kHz in both 25% and 34% exhibit irregular swinging anomalies, which vanish as temperature approaches T_m .

Figures 2(a) and 2(b) illustrate dielectric spectra of ϵ' and ϵ'' in 25% and 34% after various poling E fields at RT, in which multiple piezoelectric resonances occur between 0.2 and 1 MHz. Resonant spectra in 25% are similar for different poling fields. In 34%, resonant spectra are similar for $E \geq 5$ kV/cm. The minimum E fields to induce resonant anomalies are ~ 1.0 and ~ 2.5 kV/cm for 25% and 34%, respectively, which are smaller than their coercive fields ($E_C \sim 3.2$ kV/cm for 25% and $E_C \sim 8.0$ kV/cm for 34%). Electric hysteresis loops obtained at RT are given in Fig. 1.

Figures 3(a) and 3(b) show temperature-dependent frequency spectra of ϵ'' after poling for 25% and 34%, respectively. The resonant spectra of 25% exhibit an obvious splitting of the resonant peak (near 850 kHz) and dramatic

^{a)}Electronic mail: chien@physics.montana.edu

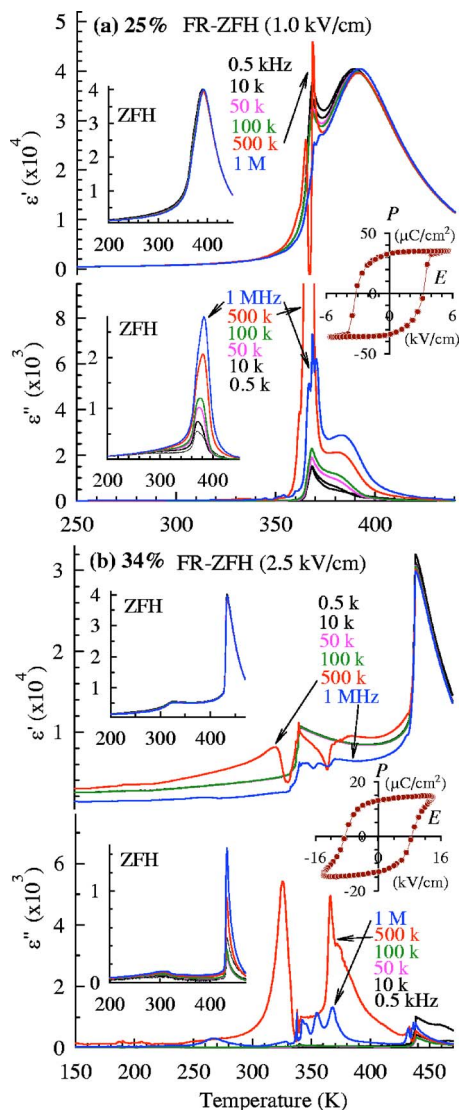


FIG. 1. (Color online) Dielectric permittivities of ZFH and FR-ZFH for (a) 25% and (b) 34%.

changes of resonant intensity at 367 K, which corresponds to an extra peak in ε' (FR-ZFH). The resonant anomaly vanishes near 380 K which is lower than $T_m \cong 390$ K. With the above data and the phase diagram for poled PMNT crystals,⁴ the poled 25% crystal likely undergoes a $R(M) \rightarrow M(R) \rightarrow C$ transition sequence near 367 and 390 K upon heating. “ $R(M)$ ” represents the dominant R domains that coexist with a smaller fraction of M domains.

The resonant spectra of ε'' in 34% show significant changes of intensity and resonant frequency near 210 and 340 K as indicated by the solid and dashed arrows, respectively, in Fig. 3(b). The resonance vanishes near 430 K, which is lower than $T_m \cong 438$ K. What are the physical origins of this behavior near 210 and 340 K? In a pure PMN crystal an extra peak was seen at $T_c \cong 212$ K in a field-heating dielectric result, and was attributed to the percolating clusters due to the suppression of the random fields.⁸ An $M(T) \rightarrow T(M)$ transition associated with a step-down anomaly near 210 K in ε' (FR-ZFH) was evidenced in (001)-cut PMNT35%.⁴ Note that the poling E field was along [111] which is the polar direction of the R phase. Thus the

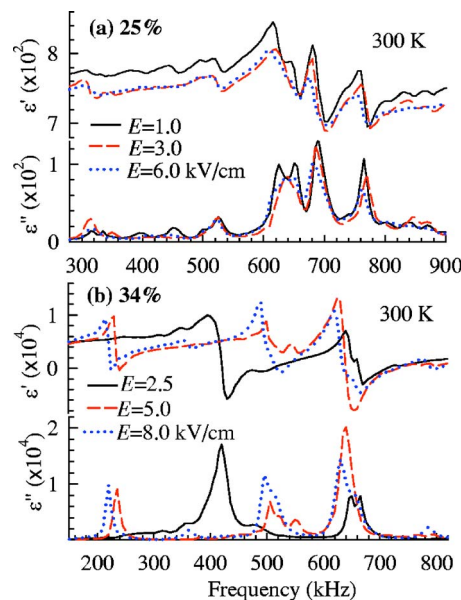


FIG. 2. (Color online) Resonant spectra after various E -field polings for (a) 25% and (b) 34%.

resonant anomaly near 210 K corresponds to a phase transformation, perhaps $R(M) \rightarrow M(R)$, associated with a long-range percolation of microdomains. Near 340 K the crystal transforms into the tetragonal phase.

What are the physical origins of piezoelectric resonances? It was found that resonant spectra can be described by the model of multiple force-damping oscillators, i.e.,

$$\begin{aligned} \varepsilon(\omega)^* &= \varepsilon'(\omega) - i\varepsilon''(\omega) \\ &= \varepsilon_c + \sum_{i=1} A_i \frac{(\omega_{0i}^2 - \omega^2) - i2\omega\gamma_i}{(\omega_{0i}^2 - \omega^2)^2 + 4\omega^2\gamma_i^2}, \end{aligned} \quad (1)$$

where $\omega_{0i}(d)$ and $A_i(d)$ are the thickness-dependent resonant frequency and amplitude for the i th oscillator, $\gamma_i(d)$ is the damping factor, and ε_c is the “clamped” dielectric permittiv-

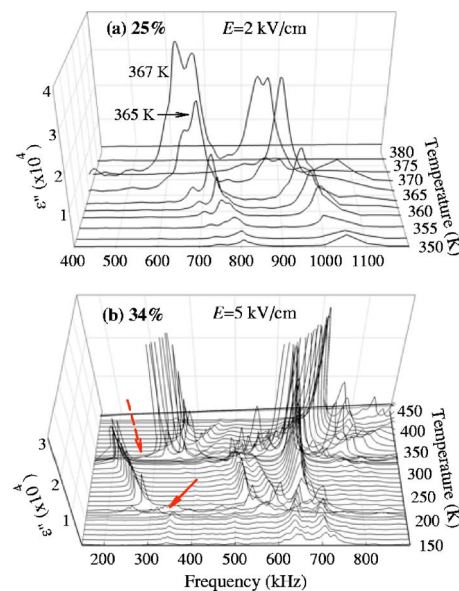


FIG. 3. (Color online) Temperature-dependent frequency spectra of ε'' after poling at 2.0 and 5.0 kV/cm for (a) 25% and (b) 34%, respectively.

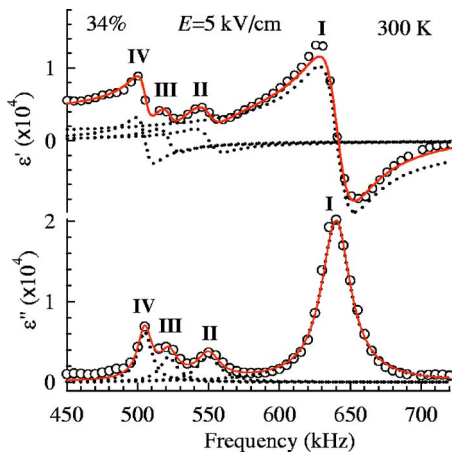


FIG. 4. (Color online) Resonant spectra of ϵ'' between 450 and 720 kHz taken at 300 K. The dotted lines are fits of Eq. (1) for peaks (I–IV) with parameters in Table I. The solid line is the sum of fittings with $\epsilon_c=2200$.

ity. The thickness dependence is included in the parameters because the piezoelectric resonance is a dimension-dependent macroscopic phenomenon, which associates with complex capacitance. To obtain Eq. (1), the ion motion was assumed to be like the one-dimensional forced damped oscillation, i.e., $d^2z/dt^2 + 2\gamma(dz/dt) + \omega_0^2z = (q/m)E_0 \text{Re}(e^{i\omega t})$, where $\gamma(d) = b(d)/2m$ and $\omega_0^2(d) = K(d)/m$. $K(d)$; $b(d)$, and m are restoring-force constant, damping coefficient, and effective ion mass, respectively. The oscillating charges can be the Pb^{+2} and $[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3]^{-2}$ ionic sublattices. A similar mathematical analysis for induced dynamic polarizability appears in Ref. 9.

The dotted lines in Fig. 4 are fitting curves of Eq. (1) with parameters given in Table I for resonant peaks (I–IV) in 34%. The consistent fittings indicate that these resonant phenomena correlate to microscopic vibrations of the ionic units. Peak ‘‘I’’ is expected to be the thickness extension (TE) mode, because its frequency increased as sample thickness was reduced. Manifold resonances are likely associated with phase segregation (due to Ti variation), various extension modes, and their higher-order overtones.

TABLE I. Fitting parameters of resonant peaks in Fig. 4.

Peak	$\omega_0/2\pi$ (kHz)	$A/4\pi^2$ (Hz ²)	$\gamma/2\pi$ (kHz)
I	640	3.2×10^{14}	1.25×10^4
II	550	3.3×10^{13}	9.5×10^3
III	522	2.4×10^{13}	7.3×10^3
IV	505	3.8×10^{13}	6.0×10^3

This work has revealed significant evidence of piezoelectric resonances in poled PMNT25% and 34% crystals, which occur in a wide temperature region. Similar resonant phenomena have also been observed in other poled PMNT $x\%$ crystals ($x=24, 26, 28, 29, 35$, and 36). Piezoelectric resonance seems to be a regular phenomenon in poled PMNT crystals and can be easily induced with poling strength less than the coercive field, but it vanishes after annealing above T_m . The dielectric resonance is sensitive to microscopic structure, and is a valuable characterization method for the PMNT system.

The authors would like to express sincere thanks to Dr. H. Luo and Y. Tang for the crystals. This work was supported by NSC Grant No. 93-2112-M-030-001 and DoD EPSCoR Grant No. N00014-02-1-0657.

- ¹T. R. Shrout, Z. P. Chang, N. Kim, and S. Markgraf, *Ferroelectr., Lett. Sect.* **12**, 63 (1990).
- ²Z.-G. Ye, B. Noheda, M. Dong, D. Cox, and G. Shirane, *Phys. Rev. B* **64**, 184114 (2001).
- ³Z. Feng, H. Luo, Y. Guo, T. He, and H. Xu, *Solid State Commun.* **126**, 347 (2003).
- ⁴C.-S. Tu, R. R. Chien, F. T. Wang, V. H. Schmidt, and P. Han, *Phys. Rev. B* **70**, 220103 (2004).
- ⁵N. Cereceda, B. Noheda, J. R. Fdez.-del-Castillo, J. A. Gonzalo, J. De Frutos, and A. M. González, *J. Eur. Ceram. Soc.* **19**, 1259 (1999).
- ⁶A. Mellinger, *IEEE Trans. Dielectr. Electr. Insul.* **10**, 842 (2003).
- ⁷X. Wei, Y. Feng, and X. Yao, *Appl. Phys. Lett.* **84**, 1534 (2004).
- ⁸V. Westphal and W. Kleemann, *Phys. Rev. Lett.* **68**, 847 (1992).
- ⁹V. D. Barger and M. G. Olsson, *Classical Electricity and Magnetism* (Allyn and Bacon, Boston, 1987), pp. 168–170.