Prior poling effect on thermal phase stability in (110)-cut Pb (Mg $1/3$ Nb $2/3$) 0.74 Ti 0.26 O 3 single crystal

R. R. Chien, V. Hugo Schmidt, Chi-Shun Tu, and F.-T. Wang

Citation: *Journal of Applied Physics* **98**, 114106 (2005); doi: 10.1063/1.2130888

View online: <http://dx.doi.org/10.1063/1.2130888>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/98/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

Field-induced intermediate orthorhombic phase in (110)-cut Pb (Mg $1/3$ Nb $2/3$) 0.70 Ti 0.30 O 3 single crystal

J. Appl. Phys. **104**, 094105 (2008); 10.1063/1.3009319

Intermediate phases in rhombohedral Pb (Mg $1/3$ Nb $2/3$) $1 - x$ Ti x O 3 crystal

J. Appl. Phys. **104**, 024110 (2008); 10.1063/1.2956611

Nanotwins and phases in high-strain Pb (Mg $1/3$ Nb $2/3$) $1 - x$ Ti x O 3 crystal

J. Appl. Phys. **103**, 074117 (2008); 10.1063/1.2904900

Dielectric, domain, and optical studies in high-Curie-temperature Pb (In $1/2$ Nb $1/2$) $1 - x$ Ti x O 3 ($x = 0.40$) single crystal

J. Appl. Phys. **100**, 104104 (2006); 10.1063/1.2387140

Effect of poling on dielectric anomalies at phase transitions for lead magnesium niobate-lead titanate crystals in the morphotropic phase boundary region

J. Appl. Phys. **99**, 064101 (2006); 10.1063/1.2179972

The image shows the cover of the AIP Applied Physics Reviews journal, featuring a diagram of a crystal structure and a graph. The background of the banner is blue with a glowing light effect and molecular models.

NEW Special Topic Sections

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

AIP Applied Physics Reviews

Prior poling effect on thermal phase stability in (110)-cut $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.74}\text{Ti}_{0.26}\text{O}_3$ single crystal

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

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

Chi-Shun Tu and F.-T. Wang

Graduate Institute of Applied Science and Engineering, Fu Jen Univeristy, Taipei 242, Taiwan

(Received 22 July 2005; accepted 6 October 2005; published online 8 December 2005)

Phases and domains in a (110)-cut $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.74}\text{Ti}_{0.26}\text{O}_3$ (PMNT26%) single crystal have been investigated as functions of temperature and dc electric (E) field by dielectric permittivity, polarizing microscopy, and electric polarization. The unpoled sample has a dominant rhombohedral (R) phase, which coexists with monoclinic (M) phase domains, i.e., R/M at room temperature. With 45 kV/cm dc poling applied along $[110]$ at room temperature, a single domain of R phase with polar orientation perpendicular to the poling field, i.e., $\underline{R}$, was obtained. After the poling was removed, the poled sample has $\underline{R}/M$ microdomains, where the M distortion is close to the R phase. The zero-field-heating domain patterns in both unpoled and poled samples exhibit continuous polarization rotation via an intrinsic M phase in the regions of 355–375 and 365–380 K, respectively. Orthorhombic and tetragonal phases were not observed in the temperature-dependent study. In general, a rhombohedral/monoclinic $\rightarrow$ monoclinic $\rightarrow$ cubic transition sequence takes place upon heating for unpoled and poled samples. © 2005 American Institute of Physics.

[DOI: [10.1063/1.2130888](https://doi.org/10.1063/1.2130888)]

I. INTRODUCTION

High-strain ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PMNT x) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PZNT x) single crystals have drawn much attention because of their superior electromechanical properties compared to lead zirconate titanate (PZT) ceramics, and therefore have great potential for designing high performance actuators and sensors.^{1–3} Many physical properties of PMNT and PZNT crystals, such as phase stability, strongly depend on titanium (Ti) content, temperature, electric (E)-field poling strength (and process), crystallographic orientation, and history.⁴ The crystal structures can occur in the cubic (C), tetragonal (T), orthorhombic (O), rhombohedral (R), monoclinic (M), and triclinic (Tri) phases. All the phases except the Tri phase have been reported in various PMNT crystals. The ultrahigh piezoelectric response has been theoretically attributed to polarization rotation induced by an external E field between T and R phases through intermediate M or O symmetries.⁵

It is believed that polarization rotation through intermediate phases plays a key role in high piezoelectric performance in PMNT materials. The correlation between polarization rotation and physical parameters, such as crystallographic orientation, temperature, and strength of external E field, is a practical issue to explore. In this report, temperature- and E -field-dependent domain structures, and dielectric permittivity, were investigated on a (110)-cut PMNT26% single crystal, because the (110)-cut crystal exhibits a sensitive movement of intermediate phase domains.

II. EXPERIMENTAL PROCEDURE

The PMNT26% single crystal was grown using a modified Bridgman method and was cut perpendicular to the $\langle 110 \rangle$ direction. The Ti concentration ($x\%$) was determined by $x = [T_m(^{\circ}\text{C}) + 10]/5$, where T_m is the dielectric maximum temperature obtained upon heating without poling. For dielectric measurement, gold electrodes were deposited on sample surfaces by dc sputtering. A Wayne-Kerr Precision Analyzer PMA3260A was used to obtain capacitance and resistance. A Janis CCS-450 cold head was used with a Lakeshore 340 controller and the ramping rate was 1.5 K/min. 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. The second process is called FR-ZFH, in which the sample was poled at room temperature (RT) before ZFH was performed below RT. The sample was annealed before ZFH measurement or before poling for FR-ZFH study. The hysteresis loops of polarization versus E field were also measured by using a Sawyer-Tower circuit at a frequency of 46 Hz.

The domain observation was studied by using a Nikon E600POL polarizing microscope mounted with a Linkam THMS600 heating/cooling stage and the experimental configuration can be found in Ref. 6. The $[001]$ orientation of the sample edge was determined by x-ray diffraction and aligned with one of the crossed polarizer/analyzer (P/A): 0° axes for domain observation so that the extinction angles shown in all domain micrographs are measured from $[001]$. To minimize the superposition of domain layers, the sample was polished to the thickness of 45 μm . Transparent conductive films of indium tin oxide (ITO) were deposited on the sample surfaces. Three different domain observations were

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

FIG. 1. (Color online) Dielectric permittivities of ZFH (without poling) and FR-ZFH (with prior poling fields at 0.75, 4.0, 12.0, and 20.0 kV/cm) measured at $f=10$ kHz. The dielectric anomalies in the region of 360–375 K are enlarged in the insets.

carried out in this study. The first is called ZFH domain observation, in which the domain structures were obtained upon heating without any E -field poling. The second process is called “ E -field-dependent” observation, in which the sample was poled at RT with increasing dc E -field strength gradually up to 45 kV/cm. The third process is a ZFH domain observation obtained 27 days later, after the second process, without thermal annealing.

III. RESULTS AND DISCUSSION

A broad dielectric maximum $T_m=390$ K and a weak shoulder (as indicated by an arrow) near 370 K, were evidenced in the ϵ' (ZFH) as shown in Fig. 1. Compared to the pure ZFH, as enlarged in the inset of Fig. 1, ϵ' (FR-ZFH) exhibits an extra sharp peak associated with weak shoulders in the region of 365–375 K for poling fields $E=0.75$ and 4.0 kV/cm. As E field increases, as seen in the inset for $E=12.0$ and 20.0 kV/cm, the extra anomalies become a single frequency independent peak near 367 K. Note that the dielectric maximum temperature T_m is not sensitive to the prior poling strength. Correspondingly, ϵ'' (FR-ZFH) also exhibits an extra sharp peak near 367 K associated with weaker peaks on both sides in the region of 365–375 K for lower poling fields. These extra “field-induced” anomalies superimpose on a broad maximum background. The minimum poling E field to induce these extra dielectric phenomena is about 0.75 kV/cm, which is less than the coercive field (~ 3.0 kV/cm) at RT as seen in Fig. 2. Similar extra field-

FIG. 2. (Color online) (a) Hysteresis loops of polarization vs E field; (b) remanent polarization vs temperature upon heating.

induced dielectric phenomena were found for other oriented, poled PMNT crystals and various Ti contents, in which the extra dielectric anomalies were contributed to the significant appearance of M phase domains.⁷

By using relations of crystallographic symmetry and optical extinction, polarizing microscopy reveals orientations of the polarizations and their corresponding phases. For interpreting domain observation among various phases by means of polarizing microscopy, a review of principles of optical extinction for (110)-cut crystal can be found in Ref. 8. For the O domains represented in Fig. 3 by open circles with no cross, the optical biaxiality of the O structure means that the extinction orientations are not known unless all three indices of refraction along the axes of the double-size ($Z=2$) O cell are known, so we cannot identify such domains by their extinction angles because we do not know these indices. Any extinctions at angles other than $0^\circ (=90^\circ)$, 35° , and 55° must be from these open-circle O , M , or Tri domains. Our large observed variation in extinction angle with temperature indicates M domains whose polarization P can vary with temperature through a large angle, whereas the direction of P is nearly fixed for a given open-circle O domain as temperature varies.

A. ZFH domain observation in the unpoled sample

As shown in Fig. 4(a) at 295 K, a larger fraction of the unpoled sample exhibits extinction at $P/A: 0^\circ$ and $85^\circ\text{--}90^\circ$, and a small fraction exhibits extinction at $P/A: 45^\circ\text{--}60^\circ$ and $35^\circ\text{--}55^\circ$. This indicates that the unpoled sample has a domi-

FIG. 3. (Color online) Projection of the optical extinction orientations on the (110) plane, which corresponds to the polarizations for various phases and domains. The solid crosses in the symbols indicate the optical electric-field axes E of the incident light for which optical extinction will occur for the corresponding domains. Measured from $[001]$, the R domains (triangles) give extinction at 0° (or 90°), 35° , and 55° . The T (squares) and O (circles with solid cross) domains also give extinction at 0° (or 90°). The extinction orientations in open circles with no cross are not known. Dashed, dash-dotted, and dotted lines represent M_A , M_B , and M_C domains, respectively.

nant R phase with polar orientation $[111]$, $[11\bar{1}]$, and/or $[\bar{1}\bar{1}1]$ that coexists with M phase domains, i.e., R/M . R/M represents more R than M phase domains. The polarizations start to rotate to $P/A: 5^\circ$, 45° – 80° , and 20° – 55° at 355 K [Fig. 4(b)]. The domain micrograph at 85° in the upper inset of Fig. 4(a), exhibiting no extinction, also indicates that the polarizations had rotated to other angles. As the temperature increases from 355 to 373 K [Figs. 4(c)–4(h)], extinction angles in the major domain matrix display a continuous change from 5° to 40° , which indicates continuous polarization rotation. The polarization rotation stops at 373 K [Fig. 4(h)] and the birefringence of the whole crystal is disappearing as temperature increases further. The crystal becomes cubic near 393 K, which is consistent with dielectric maximum temperature T_m . The continuous polarization rotation was not seen obviously by a polarizing microscope in (001)-cut PMNT26% crystal,⁷ because likely the polarization takes a certain rotation path (perhaps M_A); with that the corresponding extinction angles do not change on the (001) projection plane and do change on the (110) projection plane.

B. E -field-dependent and ZFH domain observations in the poled sample

The unpoled crystal has a R/M phase [Fig. 5(a)] at RT. As the field increases to 3.5 kV/cm, part of the domain matrix exhibits obvious change in birefringence and has extinction angles at 55° – 60° as seen in Fig. 5(b). Note that the coercive field at RT is $E_c \sim 3$ kV/cm as shown in Fig. 5(h). Based on Fig. 3, the extinction at 55° – 60° indicates appearance of another oriented R phase domain (denoted by $\bar{R}$), possibly mixed with minor M domains. The $\bar{R}$ phase domains have extinction at 55° . The possible orientations are along $[1\bar{1}1]$, $[\bar{1}\bar{1}\bar{1}]$, $[1\bar{1}\bar{1}]$, and/or $[\bar{1}11]$. The $\bar{R}$ phase domain expands with poling strength as seen in Figs. 5(c) and

FIG. 4. (Color online) ZFH domain micrographs at $P/A: 0^\circ$ obtained from the unpoled sample, where “S” represents silver paste. The insets are the domain micrographs at different P/A angles. The angles written in the domain matrix indicate the extinction angles in that area.

5(d), in which the weaving domain walls exhibit no optical extinction at all P/A angles. The whole domain matrix was dramatically affected by the poling at 4.6 kV/cm [Fig. 5(d)]. The weaving domain walls gradually disappear as E -field strength increases, as seen in Fig. 5(e). Some domain walls persist to a high field (~ 26 kV/cm) but disappear after poling at this strength for more than 3 h. The whole domain matrix almost reaches a single $\bar{R}$ phase at 45 kV/cm as shown in Fig. 5(f).

An O phase polarized along $[110]$ might be expected when such high-field poling was applied along $[110]$. There will be extinction at $P/A: 0^\circ$ if such an O phase domain exists. However, as shown in Fig. 5(f), no extinction at $P/A: 0^\circ$ was observed. Instead, the extinction appears at $P/A: 55^\circ$ [inset of Fig. 5(f)], which corresponds to the $\bar{R}$ phase. The

FIG. 5. (Color online) E -field-dependent domains observed at RT for (a) 0, (b) 3.5, (c) 4.2, (d) 4.6, (e) 15, and (f) 45 kV/cm, and (g) right after the E field was removed. (h) is hysteresis loop of polarization vs E field obtained at RT. (i)-(p) are ZFH domain structures observed 27 days later, after poling. All domain micrographs, except the insets, were taken at $P/A: 0^\circ$.

inset of Fig. 5(f) also displays the boundary of ITO electrode films. Under the poling at 45 kV/cm, microcracking was not found. After the field was removed [Fig. 5(g)], the crystal does not reestablish the R/M phase macrodomains, but instead breaks up into M/R microdomains indicated by the extinction angles 10° and 55° . About more than half of the domain matrix does not have optical extinction, perhaps due to the local stress caused by various polar microdomains.

Twenty-seven days after the field was removed, ZFH domain observation was performed. As shown in Fig. 5(i),

the crystal birefringence at RT has been changed a little, and the M domains with extinction at 10° [Fig. 5(g)] change their extinction angle to 0° – 5° and 5° – 10° . This means that the polarizations have relaxed to other M symmetries that are close to R symmetry. As temperature increases, the domain matrix exhibits an obvious change in extinction angle and birefringence near 365 K [Fig. 5(j)], which is consistent with the extra sharp anomaly observed near 367 K in both ϵ' (FR-ZFH) and ϵ'' (FR-ZFH) for the prior poling fields $E \geq 12$ kV/cm (Fig. 1). At 365 K, most domains exhibit ex-

tion at 10° and few domains at 55° , which corresponds to the M/R phase. M/R represents much more M than R phase domains. The remanent polarization, as seen in Fig. 2(b), also exhibits an apparent drop near 365 K, indicating the appearance of various oriented M phase domains.

With increasing temperature, the extinction angle changes continuously from 10° to 45° [Figs. 5(j)–5(o)], indicating that the crystal exhibits continuous polarization rotation via the M phase from 365 to 378 K. This polarization rotation through the M phase ends near 378 K. In addition, the poled sample exhibits domain boundaries [Figs. 5(i)–5(m)] between the R and M phase domains and some of these boundaries persist to ~ 373 K [Fig. 5(n)]. As temperature increases to 382 K, C the phase starts to appear [Fig. 5(o)] and no T phase is observed. The whole crystal becomes cubic near 399 K [Fig. 5(p)], where the electric polarization also approaches zero as seen in Fig. 2.

IV. CONCLUSIONS

The phase-transition sequence, $R/M \rightarrow M \rightarrow C$, takes place upon heating (ZFH) in the unpoled and poled (110)-cut PMNT26% samples. It agrees with the phase diagram of unpoled ceramic samples at RT (Ref. 9) and the phase diagram of (001)-oriented poled crystals.⁷ This study also confirms that the appearance of thermally activated M phase domains does not depend on prior poling, but the poling strength enhances the scale of the long-range-ordered M phase domains. In addition, the M phase intrinsically bridges R and C phases by means of continuous polarization rotation in the region of 355–375 K in the unpoled sample and 365–380 K in the poled sample upon heating. The difference be-

tween the unpoled and poled cases is that the M phase appears at slightly lower temperature in the unpoled sample. No O domain with polarization along $[110]$ was observed during poling along $[110]$ at any field strength up to 45 kV/cm and instead a single homogenous R phase was obtained. This is very different from the (001)-cut rhombohedral PMNT24% crystal, which exhibits networklike $[001]$ T domain chains while the poling was applied along $[001]$ at 44 kV/cm (Ref. 10). No microcracking was found in this study, which is the same as in the (001)-cut PMNT24% crystal.¹⁰

ACKNOWLEDGMENTS

The authors would like to thank Dr. Haosu Luo for the crystal. This work was supported by DoD EPSCoR Grant No. N00014-02-1-0657 and NSC Grant No. 93-2112-M-030-001.

- ¹J. Kumata, K. Uchino, and S. Nomura, *Ferroelectrics* **37**, 579 (1981).
- ²T. R. Shrout, Z. P. Chang, N. Kim, and S. Markgraf, *Ferroelectr., Lett. Sect.* **12**, 63 (1990).
- ³S.-E. E. Park and W. Hackenberger, *Curr. Opin. Solid State Mater. Sci.* **6**, 11 (2002).
- ⁴B. Noheda, *Curr. Opin. Solid State Mater. Sci.* **6**, 27 (2002).
- ⁵H. Fu and R. E. Cohen, *Nature* **403**, 281 (2000).
- ⁶C.-S. Tu, V. H. Schmidt I.-C. Shih, and R. Chien, *Phys. Rev. B* **67**, 020102(R) (2003).
- ⁷C.-S. Tu, R. R. Chien, F.-T. Wang, V. H. Schmidt, and P. Han, *Phys. Rev. B* **70**, 220103(R) (2004).
- ⁸V. H. Schmidt, R. Chien, I.-C. Shih, and C.-S. Tu, *AIP Conf. Proc.* **677**, 160 (2003).
- ⁹A. K. Singh and D. Pandey, *Phys. Rev. B* **67**, 064102 (2003).
- ¹⁰R. R. Chien, V. H. Schmidt, C.-S. Tu, L.-W. Hung, and H. Luo, *Phys. Rev. B* **69**, 172101 (2004).