J. Korean Inst. Electr. Electron. Mater. Eng.
Vol. 34, No. 5, pp. 382-385 September 2021
DOI: https://doi.org/10.4313/JKEM.2021.34.5.382
ISSN 1226-7945(Print), 2288-3258(Online)

Early Stage Report : Graduate Research

Effect of Internal Bias Field on Poling Behavior in Mn-Doped $Pb(Mg_{1/3}Nb_{2/3})O_3$-29 mol%$PbTiO_3$ Single Crystal

Geon-Ju Lee[1], Hwang-Pill Kim[1], Ho-Yong Lee[2], and Wook Jo[1]

[1] Department of Materials Science and Engineering & Jülich-UNIST Joint Leading Institute of Advanced Energy Research, Ulsan National Institute of Science and Technology, Ulsan 44919, Korea

[2] Department of Materials Science and Engineering, Sun Moon University, Asan 31460, Korea

(Received August 13, 2021; Revised August 14, 2021; Accepted August 14, 2021)

Abstract: Electrical poling is a crucial step to convert ferroelectrics to piezoelectrics. Nevertheless, no systematic investigation on the effect of poling has been reported. Given that the poling involves an alignment of spontaneous polarization, the condition for poling should be different when a material has an internal bias field that influences the domain stability. Here, we present the effect of poling profile on the dielectric and piezoelectric properties in Mn-doped $Pb(Mg_{1/3}Nb_{2/3})O_3$-29 mol%$PbTiO_3$ single crystal with an internal bias field. We showed that both the dielectric permittivity and the piezoelectric coefficient were further enhanced when the poling procedure ends with a field application along the opposite direction to the internal bias field. We expect that the current finding would give a clue to understanding the true mechanism for the electrical poling.

Keywords: Alternating current poling, Relaxor-PT single crystal, Piezoelectric single crystal, Internal bias field

Ferroelectric materials establish a spontaneous polarization with the breaking of centrosymmetry at and below the so-called Curie temperature during cooling from their manufacture. The spontaneous polarization involves a stable charge separation leading to a dipole moment. In ferroelectrics, such dipoles tend to align collectively to form a strong electric field inside the system, which increases the free energy. In the absence of an external electric field, this increase in the free energy is balanced by the formation of ferroelectric domain walls that separate the ferroelectric domains of a different orientation, i.e., a random orientation; thus, the overall vector sum of the spontaneous polarization induced internal electric field becomes zero. This means that for ferroelectric materials to be utilized for piezoelectric applications, the randomly oriented domains should be forced to align preferentially along a certain crystallographic orientation. Thanks to the features inherent to ferroelectrics, the coercive arrangement of ferroelectric domains can be achieved by the application of a fairly large electric field, which is called a 'poling' process.

It is known that the effect of electrical poling was found during the study of the dependence of dielectric permittivity on direct current (DC) bias field on $BaTiO_3$ [1,2]. This patented technique soon spread to the piezoelectric community. Jaffe et al. [3] employed a poling treatment to induce a piezoelectricity in ferroelectric lead zirconate titanates, i.e., PZT, where he applied a direct current (DC) field of 6 kV/mm for 1 h at room temperature without manifesting on which basis such poling conditions were

✉ Wook Jo; wookjo@unist.ac.kr)

chosen. Similarly, various empirical poling conditions have been employed to induce piezoelectricity onto ferroelectrics lacking physical basis [4-6], although they all are based more or less on domain switching dynamics [7]. Recent reports on the effect of alternating current (AC) poling on enhancing both dielectric permittivity and piezoelectric properties by Yamashita et al. [8,9] are rather counterintuitive, casting a question on the common understanding of poling mechanism.

It is well-known that the doping of Mn into $Pb(Mg_{1/3}Nb_{2/3})O_3$-100$x$$PbTiO_3$(PMN-100$x$PT) system induces an internal bias field that has a significant impact on the domain switching dynamics [10-12]. Likewise, it is naturally expected that the presence of internal bias field would have an influence on the poling behavior. In this report, we investigated how the polarity of electric field during poling process influences the overall functional properties of Mn-doped PMN-29PT single crystal prepared by a solid-state crystal growth (SSCG) technique.

(001)-oriented SSCG 1 mol% Mn-doped single crystals were prepared by Ceracomp Co., Ltd. The grown single crystals were cut into 5 mm x 5 mm x 0.5 mm plates. Au electrode was sputtered on 5 mm x 5 mm (001) parallel surfaces [13]. DC poling was conducted at 25℃ at 1 kV/mm for 10s. The temperature dependent dielectric permittivity was obtained between room temperature and 240℃ at 1 kHz, and frequency sweeps of impedance spectra were performed in the frequency range between 3 MHz and 6 MHz, using an impedance gain-phase analyzer (HP4194A). The piezoelectric charge coefficient d_{33} was measured by a commercial d_{33}-meter (YE2730).

The polarization hysteresis of Mn-doped PMN-29PT as in Fig. 1 reveals a considerably large internal bias field of 0.14 kV/mm in that the coercive field at the positive and negative side is 0.36 kV/mm and -0.09 kV/mm, respectively.

To polarize the Mn-doped PMN-29PT, we employed two electric field profiles as depicted in Fig. 2. One is a typical unipolar DC poling (uDCP) profile and the other is a bipolar DC poling (bDCP) profile. As summarized in the attached table, it is seen that this simple addition of a negative poling field following the usual positive poling field leads to the increase in the dielectric permittivity by 32% and in the piezoelectric coefficient by 7%.

Figure 3 depicts the temperature-dependent dielectric properties of unipolar DC poled (uDCP) and bipolar DC poled (bDCP) specimen. In the case of uDCP, two anomalies are noted. One is at ~100℃, which refers to so-called rhombohedral-to-tetragonal transition temperature, T_{RT}. The

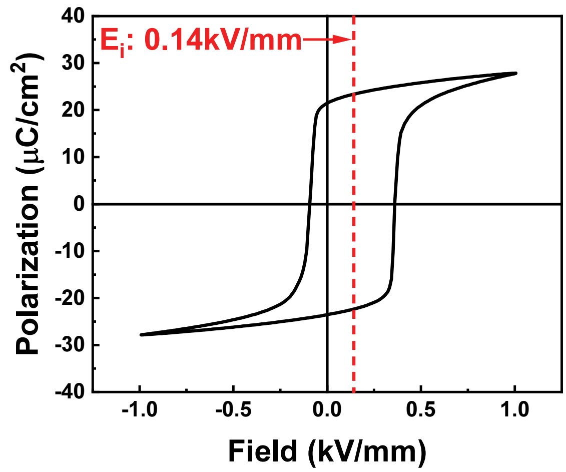
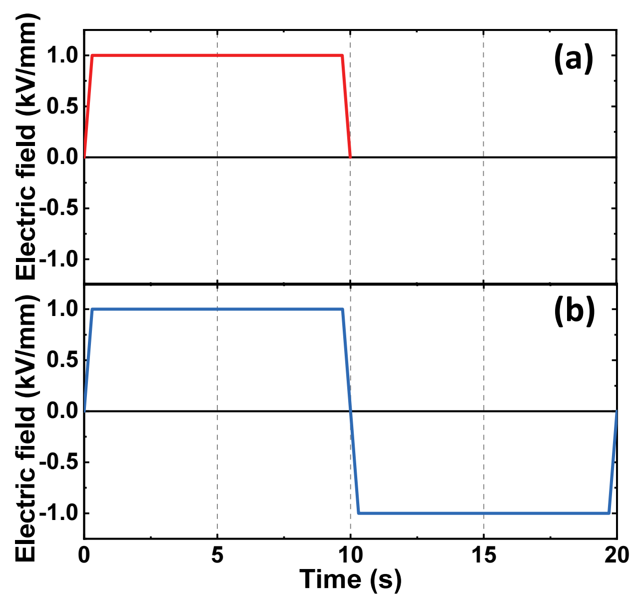


Fig. 1. Polarization hysteresis of Mn-doped PMN-29PT at 25℃.



25℃	Permittivity	d_{33}
(a) uDCP	3760	1250
(b) bDCP	4960	1350

Fig. 2. Electric field profiles employed to polarize Mn-doped PMN-29PT with resulting property set.

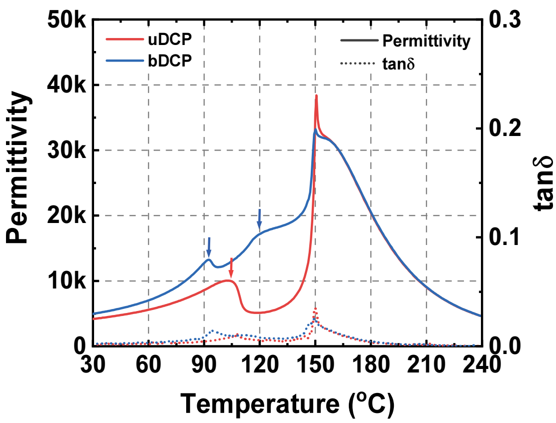


Fig. 3. Comparison of dielectric permittivity and loss as a function of temperature.

other is at 150℃, which is the Curie temperature of the system. It is interesting to note that simply applying an additional DC field along the opposite direction to the initial DC field has a huge impact on the temperature dependent dielectric behaviors. Firstly, the T_{RT} decreased from ~100℃ to ~90℃. Secondly, an additional anomaly appeared at ~120℃, while the Curie temperature remained identical.

Figure 4 presents the resonance and antiresonance spectra with the corresponding phase angle changes in the thickness mode vibration. The spectra show that the major resonance and antiresonance spectra in both uDCP and bDCP are highly convoluted by small spurious modes. A comparison between the spectra from uDCP and bDCP reveals that bDCP shifted the entire signal to lower frequencies, which implies that the domain state in the crystal may be altered.

Attempt to optimize the dielectric and piezoelectric properties by electrical poling treatment was made on Mn-doped PMN-29PT single crystal with an internal bias field. Simply with an additional field application with a reverse polarity in reference to the initial DC poling field, the dielectric permittivity and the piezoelectric coefficient were enhanced by ~32% and ~7%, respectively. The temperature dependent dielectric permittivity revealed that the so-called T_{RT} decreased with the introduction of an additional anomaly, implying that the domain state of the crystal should be altered by the additional poling treatment. This assumption was supported by the systematic shift of the impedance spectra around the resonance and antiresonance frequencies towards lower frequencies with the bipolar DCP. The exact mechanism behind this frequency shift is still unclear and requires further well-designed and detailed investigations, possibly through finite-element-method based simulations.

We showed that the presence of internal bias field has not less significant impact on the poling behavior of Mn-doped PMN-29PT single crystal, i.e., the application of a DC bias field along the opposite direction to that of the internal bias field enhances the dielectric and piezoelectric properties. Given that ceramic materials cannot be free from undesired impurities that leads to the formation of associate defects, the current results are expected to present a new insight on the effect of AC poling.

ORCID

Wook Jo https://orcid.org/0000-0002-7726-3154

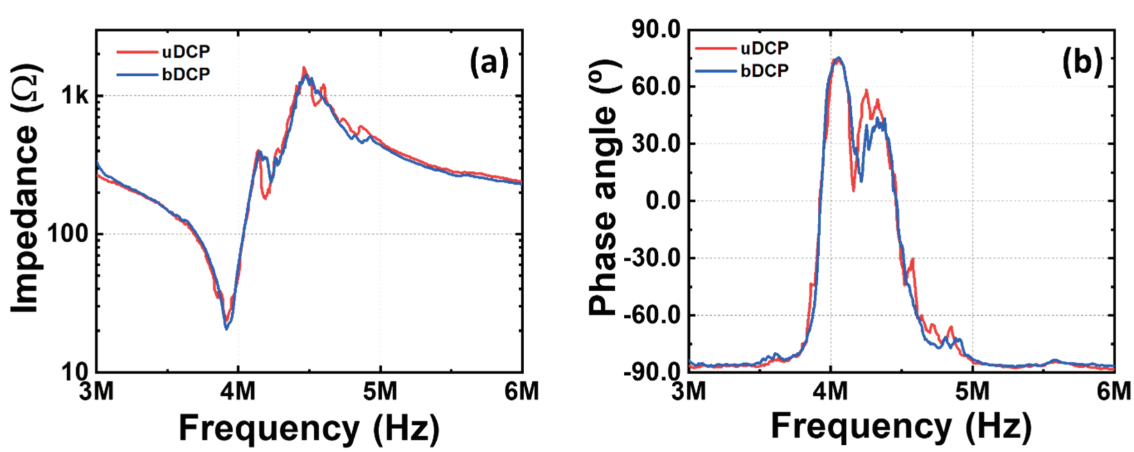


Fig. 4. Frequency sweeps of impedance and phase angle change.

ACKNOWLEDGEMENT

This research was supported by the Leading Foreign Research Institute Recruitment Program (No.2017K1A4 A3015437) through the National Research Foundation of Korea (NRF) funded by Ministry of Science and ICT.

REFERENCES

[1] C. A. Randall, R. E. Newnham, and L. E. Cross, *Materials Research Institute, The Pennsylvania State University, University Park, Pa, USA* **1** (2004).

[2] S. Wada, K. Yako, H. Kakemoto, T. Tsurumi, and T. Kiguchi, *J. Appl. Phys.*, **98**, 014109 (2005). [DOI: https://doi.org/10.1063/1.1957130]

[3] B. Jaffe, R. S. Roth, and S. Marzullo, *J. Appl. Phys.*, **25**, 809 (1954). [DOI: https://doi.org/10.1063/1.1721741]

[4] J. S. Choi, C. H. Lee, H. S. Shin, D. H. Yeo, and J. H. Lee, *J. Korean Inst. Electr. Electron. Mater. Eng.*, **31**, 19 (2018). [DOI: https://doi.org/10.4313/JKEM.2018.31.1.19]

[5] W. S. Kang, C. H. Hong, Y. J. Lee, G. Choi, D. J. Shin, D. H. Lim, S. J. Jeong, and W. Jo, *J. Korean Ceram. Soc.*, **56**, 549 (2019). [DOI: https://doi.org/10.4191/kcers.2019.56.6.03]

[6] S. W. Kim and J. H. Yoo, *Trans. Electr. Electron. Mater.*, **20**, 426 (2019). [DOI: https://doi.org/10.1007/s42341-019-00139-1]

[7] Y. A. Genenko, S. Zhukov, S. V. Yampolskii, J. Schütrumpf, R. Dittmer, W. Jo, H. Kungl, M. J. Hoffmann, and H. von Seggern, *Adv. Funct. Mater.*, **22**, 2058 (2012). [DOI: https://doi.org/10.1002/adfm.201102841]

[8] N. Yamamoto, Y. Yamashita, Y. Hosono, K. Itsumi, and K. Higuchi, (Google Patents, 2018).

[9] Y. Yamashita, N. Yamamoto, Y. Hosono, and K. Itsumi, (Google Patents, 2018).

[10] Y. H. Chen, S. Hirose, D. Viehland, S. Takahashi, and K. Uchino, *Jpn. J. Appl. Phys.*, **39**, 4843 (2000). [DOI: https://doi.org/10.1143/jjap.39.4843]

[11] H. T. Oh, H. J. Joo, M. C. Kim, and H. Y. Lee, *J. Korean Ceram. Soc.*, **55**, 166 (2018). [DOI: https://doi.org/10.4191/kcers.2018.55.2.04]

[12] A. Thakre, A. Kumar, D. Y. Jeong, G. T. Hwang, W. H. Yoon, H. Y. Lee, and J. Ryu, *Electron. Mater. Lett.*, **16**, 156 (2020). [DOI: https://doi.org/10.1007/s13391-019-00195-y]

[13] S. Zhang, F. Li, F. Yu, X. Jiang, H. Y. Lee, J. Luo, and T. R. Shrout, *J. Korean Ceram. Soc.*, **55**, 419 (2018). [DOI: https://doi.org/10.4191/kcers.2018.55.5.12]