Opinion paper

In situ total strain measurements revealing the strain mechanism of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$−PbTiO$_3$ single crystals

Hwang-Pill Kim [a], Geon-Ju Lee [a], Jae-Hyeon Cho [a], Woo-Seok Kang [a], Sang-Goo Lee [b], Ho-Yong Lee [c], Wook Jo [a, *]

[a] School of Materials Science and Engineering & Jülich-UNIST Joint Leading Institute for Advanced Energy Research, Ulsan National Institute of Science and Technology (UNIST), Ulsan, 44919, Republic of Korea
[b] IBULe Photonics, Inc., 7-39, Songdo-dong, Yeonsu-gu, Incheon, 21999, Republic of Korea
[c] Department of Materials Science and Engineering, Sun Moon University, Asan, 31460, Republic of Korea

ARTICLE INFO

ABSTRACT

The strain behavior of 0.71 Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.29 PbTiO$_3$ (PMN-PT) single crystal prepared by a solid-state single crystal growth method was investigated on two most widely used orientations, i.e., (001)- and (011)-oriented. A special emphasis was put on the correlation among longitudinal and transverse strains and the consequent volume change. We show that seemingly different strain behavior of (001)- and (011)-oriented crystals has the same origin, and the underlying mechanism excludes possible contribution from the frequently cited polarization rotation. In situ monitoring of electric field induced Poisson's ratio further suggested that the polarization vectors contributing to the strain properties in PMN-PT are not confined to a unique direction forced by the crystallographic symmetry but possess a span of angular range.

1. Introduction

Relaxor-PT single crystals represented by Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$−PbTiO$_3$ (hereafter abbreviated as PMN-PT) have drawn a great deal of attention with the unprecedentedly excellent electrochemical responses relevant for high-end devices such as high-precision actuators and high-frequency transducers [1−3]. A special emphasis has been put on their exceptionally large electric field induced strains reaching even up to ~1% [1]. This strain response is known to be observed only in the rhombohedral side of the morphotropic phase boundary (MPB). So-called a polarization rotation initially proposed by Park and Shrout has been widely supported and accepted as its working mechanism [1,4,5].

The basic idea behind the polarization rotation mechanism is that the stable spontaneous polarization direction that is pinned by the given crystal structure could be altered when an electric field high enough to overcome the free energy barrier between two stable crystallographic symmetries is applied, and its rotation

becomes highly facilitated near MPB, where the free energy landscape flattens out. The polarization rotation mechanism was readily accepted by the community, because its feasibility was well-paved by a first-principles calculation [4] and its presence was repeatedly supported by a number of in situ high intensity X-ray diffraction studies [6−9]. Apart from the inconsistency in the structural aspects especially regarding monoclinic as a bridging phase, however, the commonly practiced in situ X-ray diffraction alone cannot make a definitive evidence for the polarization rotation to operate during electrical cycles, because electric-field-induced microscopic change is too small to be properly analyzed [10]. Moreover, both phase transformation (polarization rotation) and lattice distortion (piezoelectric effect) involve a volumetric change with dimensional variations, leading to changes in X-ray diffraction profile regarding both intensity and peak position. It follows that this difference is extremely difficult to be properly resolved solely by X-ray diffraction techniques, though their physical origins are completely different.

In this work, we, instead, adopted an intuitively assessable technique, i.e., macroscopic volumetric monitoring. Given that the compressibility should increase significantly at the phase transformation leading to a sharp reduction in the Poisson's ratio, in situ

monitoring of Poisson's ratio during electrical cycle should be useful in seeing if the polarization rotation is a relevant strain mechanism for PMN-PT. In situ monitoring of Poisson's ratio revealed that at least in the PMN-PT crystals grown in solid state does not involve any discerned phase transformation during electrical cycling. As well, contrary to the common belief that the strain mechanism for (001)- and (011)-oriented crystals are different due to polarization rotation, they turned out to be the same, explaining why d_{32} is exceptionally large in (011)-oriented crystals. A comparison with the electric field induced Poisson's ratio change of a typical ferroelectric BaTiO$_3$ (BT) implied that the strain behavior of PMN-PT is a consequence of a collective motion of symmetry bridging phases, the polarization vector of which makes a range of angular distribution due to the correlated disorder at an atomic level.

2. Material and methods

(001)- and (011)-oriented 0.71 Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.29PbTiO$_3$ (PMN-29PT) single crystals were fabricated by a solid-state single crystal growth (SSCG) method by Ceracomp Co. Ltd. (Cheonan, Korea). The detail for the sample preparations can be found elsewhere [11]. The principle and the advantage of solid-state single crystal growth (SSCG) method are schematically illustrated in Fig. 1. The (001)- and (011)-oriented crystals were cut into specific combinations of orientations of [100]$_{pc}$ × [010]$_{pc}$ × [001]$_{pc}$ and [011]$_{pc}$ × [0$\bar{1}$1]$_{pc}$ × [100]$_{pc}$, respectively. Here, the subscript 'pc' refers to the pseudocubic index. The crystals with the dimension of 5 mm × 5 mm × 0.5 mm were prepared. The crystal structure was determined by X-ray diffraction (XRD: D8 ADVANCE, Bruker AXS, USA) with the CuKα radiation. We obtained the powder X-ray diffraction profile by crushing and grinding single crystals into fine powders. Before X-ray measurements, we annealed the ground powders thermally at 500 °C for 30 min to remove any residual stress induced during grinding. To measure the electrical properties of the crystals, gold electrodes were sputtered on the principal planes. Bipolar polarization hysteresis loops, P(E), were measured with the frequency of 50 mHz using a Sawyer-Tower circuit with 15 μF measurement capacitance. Bipolar longitudinal (S_3) and

transverse (S_1 or S_2) strains, S(E), were measured with three perpendicularly aligned linear variable differential transformers (LVDTs). In situ volume changes of the (001)- and (011)-crystals were calculated by $\Delta V = S_3 + 2 \cdot S_1$ and $\Delta V = S_3 + S_1 + S_2$, respectively. The index i in S_i refers to the axes defined in Fig. 2(b). The Poisson's ratio for each surface was estimated by the following equation, $\nu_{ij}^{orientation} = - S_{transverse,i}/S_{longitudinal,j}$.

3. Results and discussion

Fig. 2(a) shows the X-ray diffraction (XRD) profile of PMN-29PT powder. The insets in Fig. 2(a) present enlarged (111) and (200) peaks. The (111) peak is clearly observed to be split, while little trace of splitting but a discerned asymmetry in the (200) peak is evident. This implies that the crystal consists of a rhombohedral phase as its major component with a small fraction of a tetragonal phase (or monoclinic) [12]. Therefore, the major polarization state of the crystals is represented by eight energetically equivalent spontaneous polarization (P_S) vectors along <111> directions.

Fig. 2(b) presents possible configurations of the poling induced domain states when the poling direction is either [001] or [011]. The arrows and the grey-colored planes indicate the directions of spontaneous polarization and poling and the actual crystal surface, respectively. For the (001)-oriented single crystals, after being poled along [001], a macroscopic +4R domain symmetry is formed. The angle between the poled polarizations (+4R) and the poling direction [001] is 54.7°. In the case of the unpoled (011)-oriented crystals, there are two types of domain variants, i.e., in-plane and out-of-plane polarization vectors. The in-plane polarizations lie on the grey-colored (011) plane, while the out-of-plane domains are placed below and above the (011) plane. When poled along the [011] direction, the in-plane polarizations are transformed into one of the out-of-plane polarizations, resulting in the formation of a macroscopic +2R domain symmetry. The angle between the spontaneous polarizations (+2R) and the poling direction [011] is 35.3° which is smaller than that of the (001)-oriented crystals.

Fig. 3(a) presents the polarization hysteresis loops of the (001)- and the (011)-oriented PMN-29PT single crystal. The coercive field (E_c) of both crystals is practically the same at 0.3 kV/mm, implying
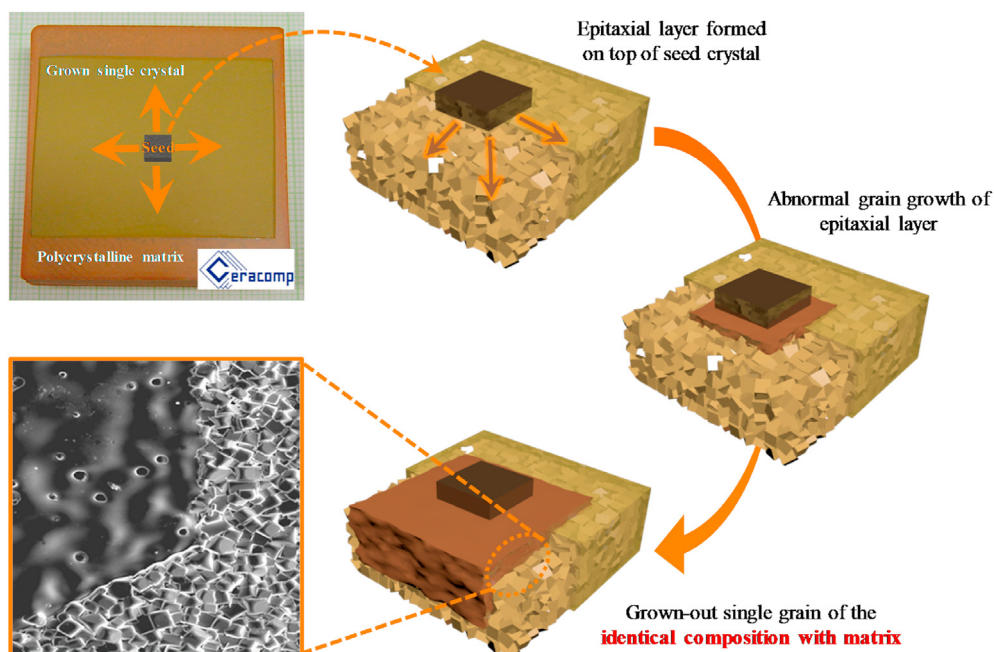

Grown single crystal

Seed

Polycrystalline matrix

Ceracomp

Epitaxial layer formed on top of seed crystal

Abnormal grain growth of epitaxial layer

Grown-out single grain of the **identical composition with matrix**

Fig. 1. Schematic illustrations of the solid-state single crystal growth (SSCG) method.
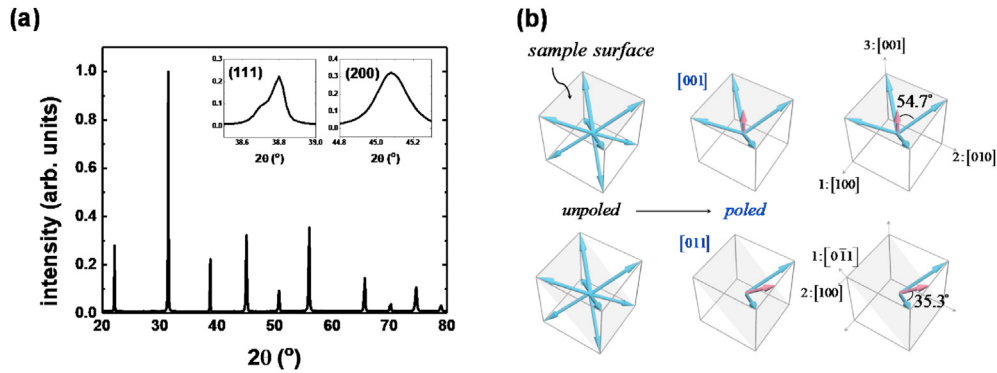
(a)

(b)

Fig. 2. (a) X-ray diffraction (XRD) pattern of PMN-29PT powder. (b) Schematic illustrations of the spontaneous polarizations and the poling direction in the (001)- and (011)-oriented crystals.

that their phase identity after being electrically polarized is identical. This means that the frequently reported electric field induced irreversible phase transformation is absent at least in our studied crystals. In fact, even the commonly referred electric field induced reversible phase transformation is missing in both crystals, which can be easily verified by the fact that the electric field induced volume change show no discontinuity during electrical cycles as demonstrated in Fig. 3(b) and (c). The polarization value of the (011)-oriented crystal is at all times higher than that of the (001)-oriented one, which is naturally expected from the angle between the crystal orientation and the polarization vector (Fig. 2(b)). Both polarization and strain in the (011)-oriented crystal show a clear

saturation behavior, best manifested by the plateau in the polarization hysteresis loops (Fig. 3(a)) and the near-zero dimensional change from above ~2 kV/mm in S_2 (Fig. 3(c)). It should be noted that should the polarization rotation operate, not only the observed such early saturation behavior but also the expansion followed by a contraction along 31 direction would not happen. In other words, this peculiar strain behaviors of the (011)-oriented crystal is a strong evidence for the absence of any phase transformation under electrical loading.

As noted, (011)-oriented single crystals have their importance due to the exceptionally large d_{32} and the consequent large S_2 [13], though the underlying mechanism is still not given. Attention may

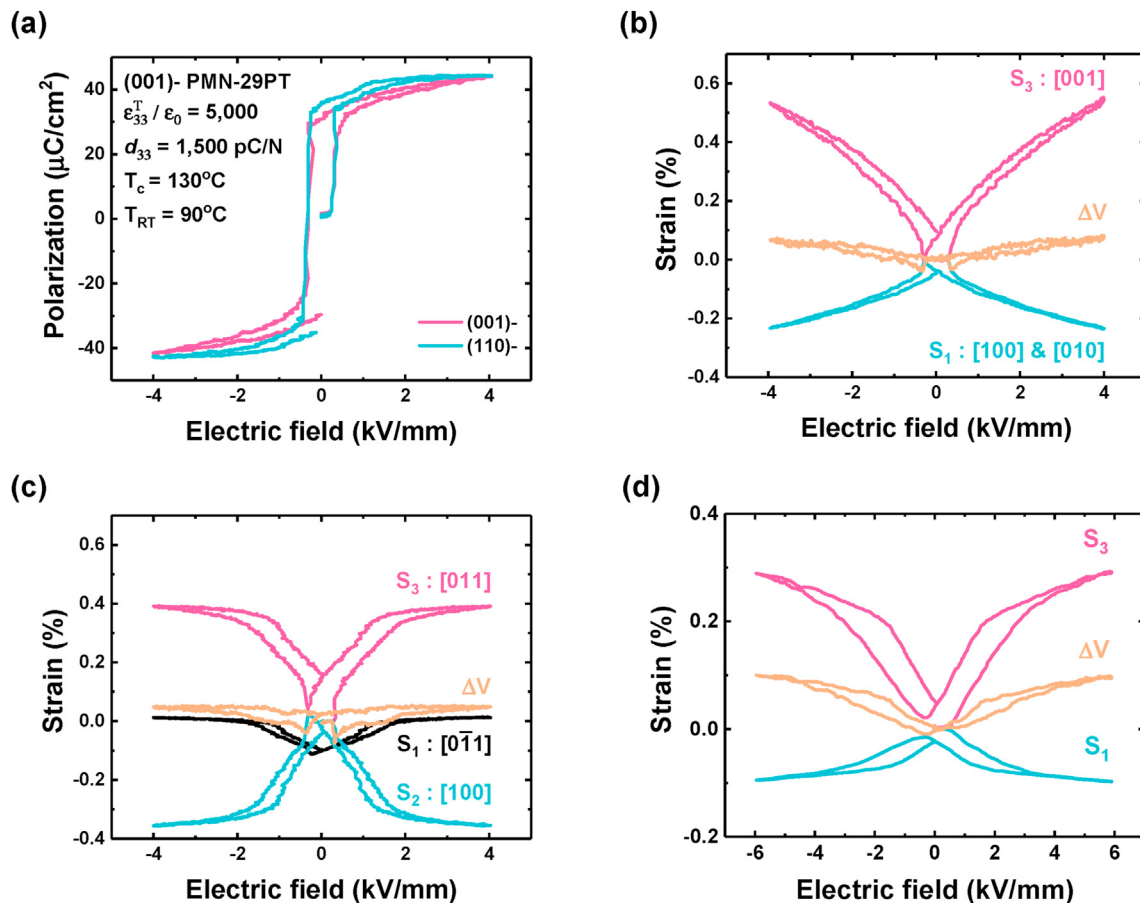**(a)**

(b)

(c)

(d)

Fig. 3. (a) Polarization hysteresis loops of (001)- and (011)-oriented PMN-29PT single crystals. Bi-polar longitudinal strains, transverse strains and volume changes of the (b) (001)-oriented PMN-29PT single crystals, (c) (011)-oriented PMN-29PT single crystals, and (d) BaTiO$_3$ (BT) ceramic.

be paid to the strain behaviors of (011)-oriented crystal as in Fig. 3(c), visualizing why (011)-oriented crystal has an exceptionally large d_{32} (S_2). Different from the (001)-oriented crystal, where only S_3 expands but the other two strain components contract, both S_1 and S_3 expand to further contract S_2 in the (011)-oriented crystal. One can see that electrical cycles do not cause any significant volume change; thus, $\Delta V = S_1 + S_2 + S_3 \approx$ constant. In other words, it can be said that (001) and (011) orientation are the optimized configuration for maximizing d_{33} and d_{32}, respectively.

On the other hand, one can notice that the profile of the volume change during electrical cycles resembles that of the longitudinal strain in terms of the hysteresis and the discontinuous contraction during switching. The presence of hysteresis in the volume change is attributed to a hydrostatic piezoelectric contribution (d_h) which enhances and retards, respectively, the longitudinal and the transverse strain change during electrical loading but acts the other way around during electrical unloading. Fig. 3(d) shows the change in the longitudinal, the transverse, and the volume during electrical cycling of typical ferroelectrics, exemplarily shown with BT ceramic. It is interesting to note that the strain behavior of (001)-oriented single crystal is practically the same with that of BT, strongly supporting our claim that the strain behavior of our (001)-oriented PMN-0.29 PT is free of electric-field-induced phase transformation despite the highly compatible large piezoelectric properties.

Fig. 4(a) and Fig. 4(b) display the Poisson's ratio of the (001)- and the (011)-oriented single crystals during a bipolar poling cycle. Given that S_1 is identical with S_2 in the case of the (001)-oriented crystal, the Poisson's ratio is simply given by $\nu_{13}^{001} = -S_1/S_3 = 0.5(1 - S_h/S_3)$ (S_h refers to the hydrostatic strain, which is equal to ΔV), and shown to asymptotically approach 0.4 starting from 0.5 at E_c. Here, the Poisson's ratio of 0.4 was determined by the ratio between the saturation S_3 and S_h by extrapolation. The Poisson's ratio of 0.5 means the polarization switching is dominated by domain wall motion, since domain wall motion is, in principle, an isochoric process, i.e., $S_h = 0$. This means that the value of 0.4 is for the Poisson's ratio of the intrinsic piezoelectric effect. It is noted that the unreasonably large positive spiking during switching at around $\pm E_c$ is not a factual observation but an artifact due to the lower resolution limit of the used LVDT sensors. The gradual change in the Poisson's ratio from 0.5 to 0.4 implies that the currently observed piezoelectric strain is the result of a mixed contribution from the domain wall motion mostly dominant at E_c and the intrinsic piezoelectric effect gradually significant as the electric field increases.

Fig. 4(b) shows the electric field dependent changes in the Poisson's ratio measured along the principal axes. It is interesting to see that ν_{23} and ν_{13} respectively approach 0.84 and −0.04 making their average 0.4, which is identical with that of ν_{13}^{001}. The current result suggests that the strain mechanism for both (001)- and (011)- oriented crystal is the same in principle, i.e., no phase transformation assisted.

Fig. 4(c) and (d) compare the change in the Poisson's ratio of PMN-29PT single crystals and BT ceramic during a bipolar cycle. We draw your attention to the fact that the point of the maximum electric field (E_{max}) do not match that of the minimum Poisson's ratio (ν_{min}) in PMN-29PT, while they are identical in BT. At the moment, we do not have concrete evidences to explain the difference straightforward, but we noted that the mismatch between E_{max} and ν_{min} could result, when the electric field causes a collective motion of polarization vectors of slightly different orientations. In fact, the polarization vectors in relaxor-based crystals exemplarily PMN-based have a range of spatial distribution due to the randomly populated different types of aliovalent cations in B site as we and
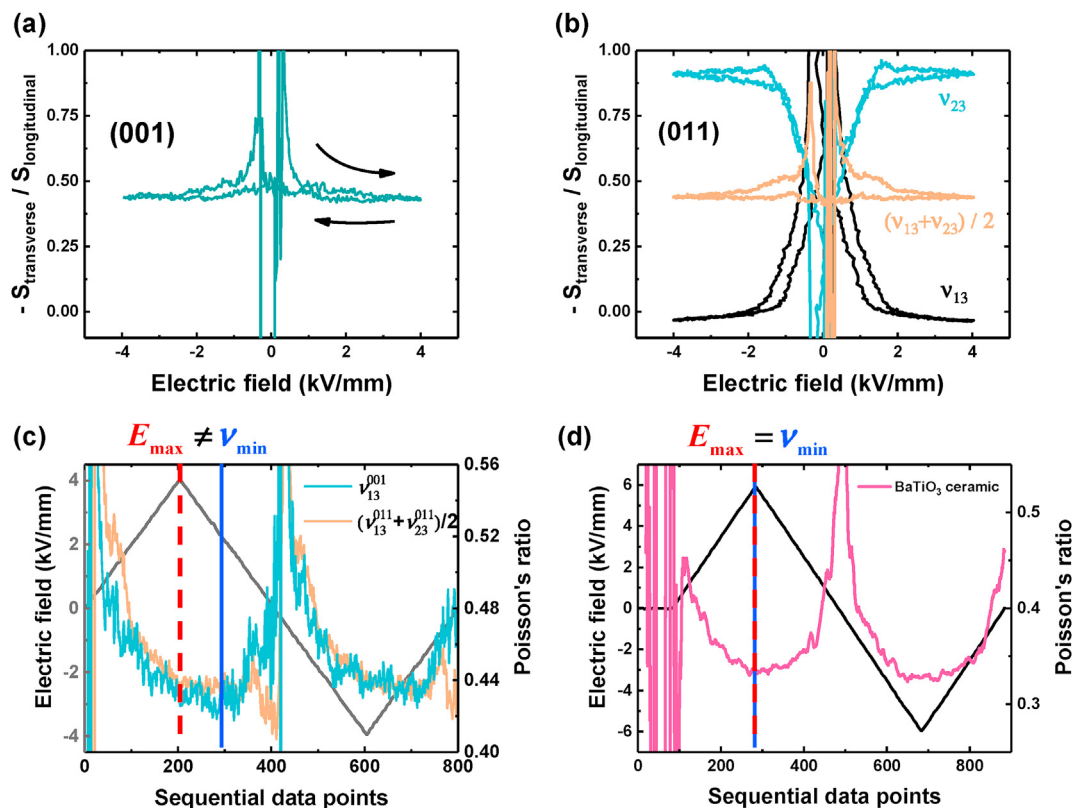

Fig. 4. Changes in the Poisson's ratio of (a) (001)- and (b) (011)-oriented single crystals during a bipolar poling cycle. Variations in the Poisson's ratio of the (c) PMN-29PT single crystals and (d) BaTiO₃ (BT) ceramic as a function of a bipolar electric field signal.

others experimentally observed and termed as 'symmetry bridging phases' [14,15]. However, the polarization vectors in the representative normal ferroelectric BT is strictly bound to its crystal symmetry. Further investigation is in progress to support the proposed mechanism.

4. Conclusions

The volume change of (001)- and (011)-oriented PMN-PT single crystals during electrical cycles was monitored by simultaneously measuring longitudinal and transverse strain. Both volume change and calculated Poisson's ratio clearly indicate that the strain mechanism of two differently oriented single crystals is the same, which is a counter-intuitive with a view to the commonly accepted polarization rotation mechanism. It was proposed that the exceptionally high strain properties of PMN-PT single crystals come from a collective motion of symmetry bridging phase, the polarization direction of which has a range of angular distribution, under electrical loading.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

References

[1] Park S-E, Shrout TR. Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals. J Appl Phys 1997;82:1804–11.

[2] Hong C-H, Kim H-P, Choi B-Y, Han H-S, Son JS, Ahn CW, Jo W. Lead-free piezoceramics — where to move on? J Materiomics 2016;2:1–24.

[3] Kim H-P, Ahn CW, Hwang Y, Lee H-Y, Jo W. Strategies of A Potential importance, making lead-free piezoceramics truly alternative to PZTs. J Korean Ceram Soc 2017;54:86–95.

[4] Fu H, Cohen RE. Polarization rotation mechanism for ultrahigh electromechanical response in single-crystal piezoelectrics. Nature 2000;403:281–3.

[5] Noheda B. Structure and high-piezoelectricity in lead oxide solid solutions. Curr Opin Solid St M 2002;6:27–34.

[6] Fan L, Chen J, Ren Y, Pan Z, Zhang L, Xing X. Unique piezoelectric properties of the monoclinic phase in $Pb(Zr,Ti)O_3$ ceramics: large lattice strain and negligible domain switching. Phys Rev Lett 2016;116:027601.

[7] Liu H, Chen J, Fan L, Ren Y, Pan Z, Lalitha KV, Rodel J, Xing X. Critical role of monoclinic polarization rotation in high-performance perovskite piezoelectric materials. Phys Rev Lett 2017;119:017601.

[8] Liu H, Chen J, Huang H, Fan L, Ren Y, Pan Z, Deng J, Chen LQ, Xing X. Role of reversible phase transformation for strong piezoelectric performance at the morphotropic phase boundary. Phys Rev Lett 2018;120:055501.

[9] Hou D, Usher T-M, Fulanovic L, Vrabelj M, Otonicar M, Ursic H, Malic B, Levin I, Jones JL. Field-induced polarization rotation and phase transitions in $0.70Pb(Mg_{1/3}Nb_{2/3})O_3-0.30PbTiO_3$ piezoceramics observed by in situ high-energy x-ray scattering. Phys Rev B 2018;97:214102.

[10] Gorfman S, Schmidt O, Tsirelson V, Ziolkowski M, Pietsch U. Crystallography under external electric field. Z Anorg Allg Chem 2013;639:1953–62.

[11] Oh H-T, Joo H-J, Kim M-C, Lee H-Y. Effect of Mn on dielectric and piezoelectric properties of 71PMN-29PT [$71Pb(Mg_{1/3}Nb_{2/3})O_3$-29PbTiO_3$] single crystals and polycrystalline ceramics. J Korean Ceram Soc 2018;55:166–73.

[12] Noheda B, Cox DE, Shirane G, Gao J, Ye ZG. Phase diagram of the ferroelectric relaxor$(1-x)PbMg_{1/3}Nb_{2/3}O_3-xPbTiO_3$. Phys Rev B 2002;66:054104.

[13] Peng J, Luo H-S, Lin D, Xu H-Q, He T-H, Jin W-Q. Orientation dependence of transverse piezoelectric properties of $0.70Pb(Mg_{1/3}Nb_{2/3})O_3-0.30PbTiO_3$ single crystals. Appl Phys Lett 2004;85:6221–3.

[14] Kim H-P, Lee G-J, Jeong HY, Jang J-H, Kim G-Y, Choi S-Y, Lee H-Y, Lee S-G, Jo W. Symmetry-bridging phase as the mechanism for the large strains in relaxor-PbTiO_3$ single crystals. J Eur Ceram Soc 2019;39:3327–31.

[15] Sun Y, Karaki T, Jujii T, Yamashita Y. Alternate current poling and direct current poling for $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$ single crystals. Jpn. J. Appl. Phys. 2019;58(SL):SLLC06. https://doi.org/10.7567/1347-4065/ab389c.

Hwang-Pill Kim is currently a combined M.S./Ph.D. candidate in the School of Materials Science and Engineering at Ulsan National Institute of Science and Technology (UNIST), Ulsan, Republic of Korea. He got his B.S degree in Material Science and Engineering in 2015 from UNIST. His research field is about the engineering of ferroelectric domains in piezoelectric single crystals under the supervision of Prof. Wook Jo.

Geon-Ju Lee is currently the Ph.D. candidate in the School of Materials Science and Engineering at Ulsan National Institute of Science and Technology (UNIST), Ulsan, Republic of Korea. He got his M.S degree in Material Science and Engineering in 2020 from UNIST. His research field is about the Poling effects on piezoelectric single crystals under the supervision of Prof. Wook Jo.

Jae-Hyeon Cho is currently the combined M.S./Ph.D. candidate in the School of Materials Science and Engineering at Ulsan National Institute of Science and Technology (UNIST), Ulsan, Republic of Korea. He got his B.S degree in Material Science and Engineering, in 2017, from UNIST. His research field is about the ceramic processing and characterizations for developing single-phase magnetoelectric multiferroic materials.

Woo-Seok Kang is currently the Ph.D. candidate in the School of Materials Science and Engineering at Ulsan National Institute of Science and Technology (UNIST), Ulsan, Republic of Korea. He got his M.S degree in Department of Electrical and Electronics Engineering in 2015 from Chung-Ang University, Seoul, Republic of Korea. He researched on texturing effect on piezo-sensor/piezo-actuator for 3 years in MODA-INNOCHIPS Co., Ltd. His research field is about enhancing the piezoelectric and dielectric properties of ceramic materials through the Templated Grain Growth (TGG) technology under the supervision of Prof. Wook Jo.

Sang-Goo, Lee received his Ph.D. from Seoul National University (SNU, Korea) in 1995. After Ph. D., he worked on the control of crystal morphology and size in various reaction systems as a Manager of Process Development Team at HANWHA Corp. (Aug. 1995–Sept., 1997). He had handled the growth of relaxor ferroelectric (PMN) single crystal which is a very important material for electrostrictive, electro-optic devices at CMR, Stanford Univ. (1997.10–1999). And the research result of this process was presented on the Applied Physics Letter at 1999. Since August of 1999, he founded iBULe Photonics in Korea, a new material development company for commercializing this material. And it is in a leading position to develop and produce piezoelectric PMN-PT / PIN-PMN-PT single crystal materials, wafers, and applications with patented technology. iBULe Photonics now produces PMN-PT/PIN-PMN-PT and adopts it to its new products; medical ultrasound probe, SONAR sensor, NDT, accelerometer, flame detector and energy harvest and so on. Recently, he is finding a research team for developing a new concept of integrated systems for diagnosis and treatments.

Ho-Yong Lee is a Professor in the Department of Materials Science and Engineering at Sunmoon University. He received a B.E. degree in Mineralogy and Petroleum from Seoul National University in 1987 and his Ph.D. in Materials Science and Engineering in 1993. He developed the "solid-state single crystal growth (SSCG) technique" for ferroelectric/piezoelectric materials such as $BaTiO_3$, $Ba(Ti,Zr)O_3$, PMN-PT, and PMN-PZT. In 2000, he founded a venture company (Ceracomp Co., Ltd. [www.ceracomp.com]) to commercialize the SSCG technique. His research interests focus on the fabrication, characterization, and application of high performance ferroelectric/piezoelectric single crystals.

Dr. Wook Jo is a Professor at the School of Materials Science and Engineering and the head of Jülich-UNIST Joint Leading Institute for Advanced Energy Research, Ulsan National Institute of Science and Technology (UNIST), Ulsan, Korea. Prior to joining the faculty of UNIST in 2014, he had served as a group leader for the Processing of Ferroelectrics lab, Technische Universität Darmstadt, Germany as of 2007. His recent research focuses on the functional properties of ferroelectric materials with a special emphasis on the lead-free piezoceramics and relaxor ferroelectrics as well as processing and characterization of room-temperature ferromagnetically-coupled ferroelectrics. He has published over 150 research papers in refereed international journals and 7 books, and holds 8 patents.