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1 **Critical Role of Monoclinic Polarization Rotation in High-performance**  
2 **Perovskite Piezoelectric Materials**

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12

1 **Abstract**

2 High-performance piezoelectric materials constantly attract the interest both for  
3 technological applications and fundamental research. The understanding of the origin  
4 for the high-performance piezoelectric property remains a challenge mainly due to the  
5 lack of direct experimental evidence. We have performed in-situ high-energy X-ray  
6 diffraction combined with 2D geometry scattering technology to reveal the underlying  
7 mechanism for the perovskite-type lead-based high-performance piezoelectric  
8 materials. The direct structural evidence has revealed that the electric-field-driven  
9 continuous polarization rotation within the monoclinic plane plays a critical role to  
10 achieve the giant piezoelectric response. An intrinsic relationship between crystal  
11 structure and piezoelectric performance in perovskite ferroelectrics has been  
12 established: A strong tendency of electric-field-driven polarization rotation generates  
13 peak piezoelectric performance and vice versa. Furthermore, the monoclinic  $M_A$   
14 structure is the key feature to superior piezoelectric properties as compared to other  
15 structures such as monoclinic  $M_B$ , rhombohedral and tetragonal. High piezoelectric  
16 response originates from intrinsic lattice strain, but little from extrinsic domain  
17 switching. The present results will facilitate designing high-performance perovskite  
18 piezoelectric materials by enhancing the intrinsic lattice contribution with easy and  
19 continuous polarization rotation.

20

1 Piezoelectric materials, which convert mechanical energy into electrical energy and  
2 vice versa, are crucial in modern applications for electromechanical devices. Most of  
3 the high-performance piezoelectric materials have perovskite structure and form a  
4 morphotropic phase boundary (MPB) with tetragonal  $\text{PbTiO}_3$ , such as  
5  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - $\text{PbTiO}_3$ ,  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  and their ternary systems [1,2]. Recently, there  
6 has been considerable interest in developing lead-free piezoelectric materials [3-5].  
7 However, no lead-free alternatives have been found that can completely replace the  
8 lead-based materials until now. To overcome this situation, it is essential to  
9 understand the origin of high-performance of piezoelectricity.

10 Several theories have been put forward to achieve this goal. Firstly, the coexistence  
11 of tetragonal (T) and rhombohedral (R) phases near the MPB region has been  
12 proposed to enhance the piezoelectric property by enabling more switchable  
13 polarization directions or the additional interphase transformation [1,6-8]. In 1999,  
14 Noheda *et al* discovered the important low symmetry monoclinic (M) structure in  
15  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  [9], which has also been corroborated in other systems [10-13].  
16 High piezoelectric response was assigned to the polarization rotation mechanism  
17 [2,14,15]. The polarization rotation path via an intermediate monoclinic among  
18 tetragonal, rhombohedral, orthorhombic phases has been intensively studied for  
19 various lead-based piezoelectrics [11-13,16-19]. The monoclinic phase is believed to  
20 be the bridge of polarization between morphotropic phases and provides for a flexible  
21 polarization rotation [11,12,14,15]. The high-performance piezoelectricity is mainly  
22 attributed to the large shear piezoelectric response [13,20,21] which is considered to  
23 be directly linked to polarization rotation [22]. Especially, the thermodynamic

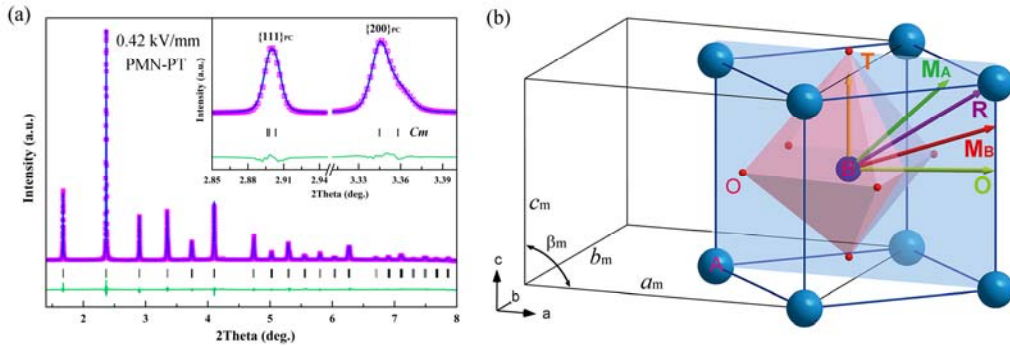
1 analysis has elucidated the polarization rotation as a consequence of the flattening of  
2 the free energy profile near the MPB [22,23]. In addition, mesoscopic models have  
3 also been proposed, such as the nanodomain and adaptive ferroelectric phase state  
4 [24,25].

5 However, no direct structural proof has been provided for the continuous  
6 polarization rotation and its intrinsic correlation to high-performance piezoelectricity.  
7 Recently, we have employed the method of in-situ high-energy synchrotron X-ray  
8 diffraction (SXRD) combined with 2D scattering geometry, which affords the  
9 possibility to simultaneously extract the information of crystal structure, domain  
10 switching, and lattice strain of piezoelectric materials [18].

11 In this Letter, we have studied several lead-based piezoceramic systems with high  
12 or moderate performance by in-situ high-energy SXRD. Phase structure, domain  
13 switching and in particular, the process of polarization rotation are analyzed as  
14 function of electric field. The present study reveals the unique polarization rotation  
15 within the  $(110)_{PC}$  plane of the monoclinic phase, and delivers direct structural  
16 evidence for the giant piezoelectric response. The summary of the intrinsic  
17 structure-property correlation will be helpful for designing new high-performance  
18 piezoelectric materials in the future.

19 Several lead-based piezoceramic systems have been fabricated by solid-state  
20 reaction method, which include both high and moderate performance. The  
21 high-performance systems are  $0.675\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.325\text{PbTiO}_3$  (PMN-PT,  $d_{33} =$   
22  $670$  pC/N),  $0.41\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.23\text{PbZrO}_3\text{-}0.36\text{PbTiO}_3$  (PNN-PZT,  $d_{33} =$   
23  $650$  pC/N),  $0.128\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.336\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.536\text{PbTiO}_3$  (PMN-PNN-PT,

1  $d_{33} = 600$  pC/N). A moderate-performance system was included with  
 2  $0.33\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.67\text{PbTiO}_3$  (PNN-PT,  $d_{33} = 400$  pC/N). By using the present  
 3 method of in-situ high-energy SXRD technology combined with appropriate 2D  
 4 scattering geometry (see Fig. S1(a), of the Supplemental Material [26]), the  
 5 diffraction patterns at the  $45^\circ$  sectors contain negligible effects of preferred  
 6 orientation, which allows extracting the important piezoelectric-related structure  
 7 information, such as the polarization rotation behavior. This strategy to minimize the  
 8 effect of preferred orientation is analogous to the important method reported by  
 9 Hinterstein *et al.* [16,36]. The in-situ diffraction data were collected during the  
 10 unloading procedure from an electric field near the coercive field ( $E_C$ ) to zero electric  
 11 field ( $E = 0$  kV/mm). More experimental details are provided in the Supplemental  
 12 Material [26].



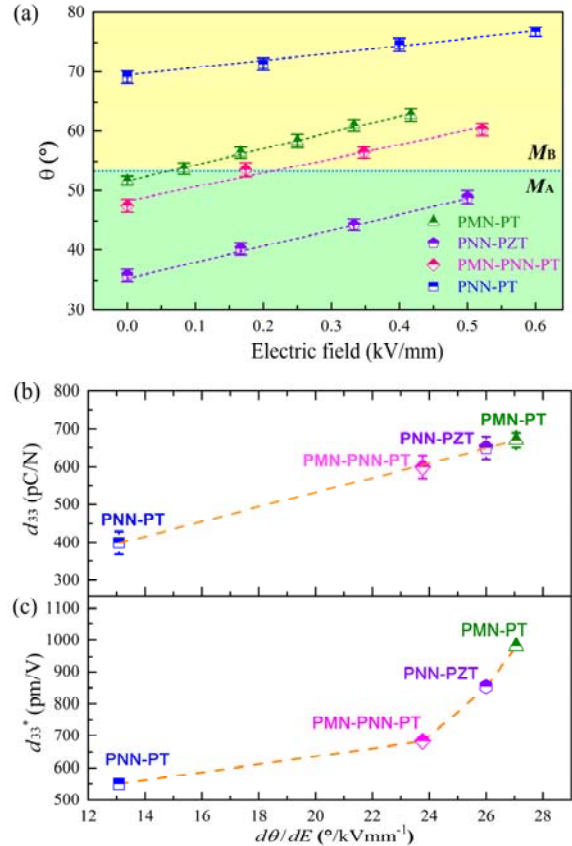
13  
 14 FIG. 1. (a) Full-profile Rietveld refinement of the monoclinic phase of PMN-PT at the  
 15  $45^\circ$  sector under 0.42 kV/mm. The observed data (pink points), the calculated profile  
 16 (blue line), and the difference between the observed and calculated patterns (bottom  
 17 green line) are depicted. The thick marks indicate the Bragg peak positions of the  $C_m$   
 18 phase. The inset provides the enlarged profiles of  $\{111\}_{PC}$  and  $\{200\}_{PC}$ . (b) Schematic

1 illustration for the polarization vectors in the  $(110)_{PC}$  plane of monoclinic ( $Cm$ ) and  
2 other phases.  $M_A$ ,  $M_B$ , T, R and O specifies monoclinic  $M_A$ , monoclinic  $M_B$ ,  
3 tetragonal, rhombohedral, and orthorhombic structures, respectively.

4 It is intriguing to note that after electric field poling a single monoclinic phase has  
5 been achieved for all four piezoceramic systems of PMN-PT, PNN-PZT,  
6 PMN-PNN-PT and PNN-PT. Here, we focus on determination of the electric-field  
7 induced monoclinic phase. Firstly, according to the high angle  $\{400\}_{PC}$  profile with  
8 the character of two distinct peaks (Fig. S4 of Ref. [26]), and the asymmetry of the  
9  $\{222\}_{PC}$  profile as function of azimuthal angle (Fig. S5 of Ref. [26]), the tetragonal,  
10 rhombohedral and orthorhombic phase could be tentatively excluded. The results of  
11 Rietveld refinement show that the monoclinic ( $Cm$ ) phase yields the best agreement.  
12 For instance, for PMN-PT ceramic at 0.42 kV/mm [Fig. 1(a)], the agreement factor is  
13  $R_{wp} = 3.26\%$  for the  $Cm$  model, while worse refinements were achieved in other  
14 models such as  $R3m$ ,  $P4mm$ ,  $P4mm+R3m$ ,  $Pm$ , and  $Bmm2$  with higher  $R_{wp}$  values of  
15 4.14%, 3.46%, 3.43%, 3.46% and 3.47%, respectively (Table S1 of Ref. [26]).  
16 Accordingly, it can be confirmed that a single monoclinic phase ( $Cm$ ) exists for the  
17 present studied piezoelectric systems. Extensive details on structure analysis are  
18 provided in the Supplemental Material [26].

19 Even though all these piezoceramic systems exhibit the same monoclinic structure  
20 ( $Cm$ ), it is interesting to observe that there is a definitive difference in polarization  
21 behavior. The high-performance systems of poled PMN-PT, PNN-PZT and  
22 PMN-PNN-PT exhibit  $M_A$  polarization behavior at 0 kV/mm, while the

1 moderate-performance PNN-PT displays  $M_B$  behavior [Fig. 1(b)]. A common feature  
 2 of  $M_A$  and  $M_B$  is that the polarization is constrained within the  $(110)_{PC}$  plane, but the  
 3 difference is that the monoclinic  $M_A$  has the polarization lying between  $[001]_{PC}$  and  
 4  $[111]_{PC}$  directions which acts as a bridge between T and R phase, while the  
 5 polarization of the  $M_B$  phase lies between the  $[110]_{PC}$  and  $[111]_{PC}$  directions which  
 6 acts as a bridge between O and R phases [19]. Here, we define the angle between the  
 7 polarization vector and the  $[001]_{PC}$  direction as  $\theta$  (Fig. S9 of Ref. [26]). It is easy to  
 8 see that when  $\theta$  around is  $0\sim 54.7^\circ$ , it is in the  $M_A$  region, while  $\theta$  around  $54.7^\circ\sim 90^\circ$   
 9 belongs to the  $M_B$  region.



10

11 FIG. 2. (a) The angle of polarization vector as function of electric field ( $\theta$  vs.  $E$ ). The



1 boundary of  $M_A$  and  $M_B$  phases is indicated by the dashed line. (b) The macroscopic  
2 measured piezoelectric coefficient  $d_{33}$ , and (c) the calculated piezoelectric coefficient  
3  $d_{33}^*$  from intrinsic lattice strain as a function of  $d\theta/dE$ .

4 After performing the full-profile Rietveld refinements for four monoclinic  
5 piezoelectric systems at various electric fields, the electric field-driven polarization  
6 properties can be obtained. The present study reveals critical evidence of the electric  
7 field-driven continuous polarization rotation,  $\theta$  vs.  $E$  [Fig. 2(a)]. At 0 kV/mm, all the  
8 three piezoceramic systems of PMN-PT, PNN-PZT, PMN-PNN-PT with relatively  
9 higher  $d_{33}$  exhibit the  $M_A$  phase, but PNN-PT with relatively lower  $d_{33}$  features the  $M_B$   
10 phase. Upon increasing electric field, electric-field-driven continuous polarization  
11 rotation sets in, which has never been observed before. For the PNN-PZT and  
12 PNN-PT, they remain in the same monoclinic region. However, there is an  
13 electric-field-driven  $M_A$ -to- $M_B$  polarization transformation for the PMN-PT and  
14 PMN-PNN-PT. Note that in the  $0.65\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.35\text{PbTiO}_3$  single crystals, the  
15 monoclinic  $M_A$  structure has been observed under applied weak electric field [10].

16 The value of polarization can be estimated by considering a purely ionic state. The  
17 magnitude of polarization in four piezoelectric systems almost maintains unchanged  
18 in the studied electric field range (Fig. S10 of Ref. [26]), which indicates that electric  
19 field drives the rotation but not the magnitude change of polarization vectors.

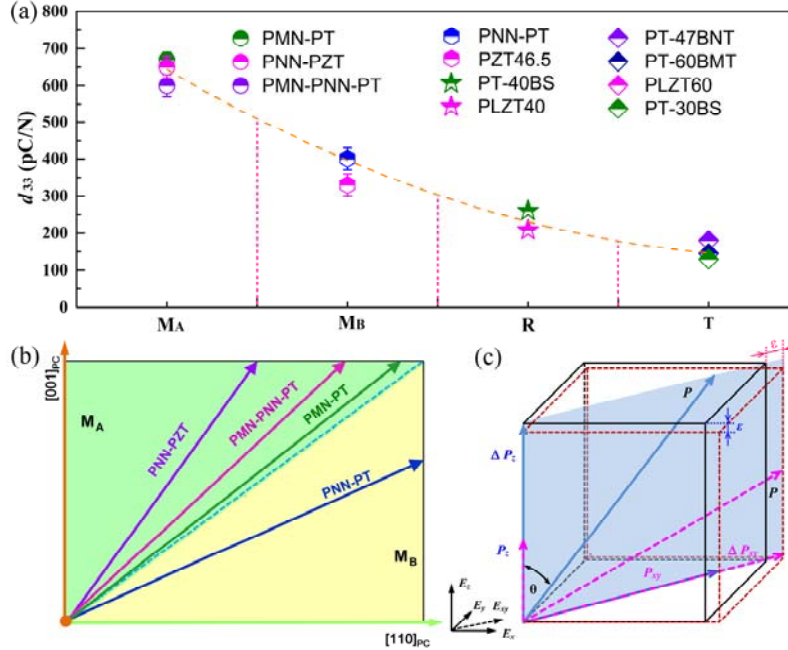
20 As displayed in Fig. 2(a), there is a linear relationship for  $\theta$  vs.  $E$ . Here, the slope is  
21 defined as  $d\theta/dE$ . A large value of  $d\theta/dE$  defines extensive electric-field-driven  
22 polarization rotation, while a small one describes limited polarization rotation. There

1 is significant difference in the  $d\theta/dE$  for the four piezoelectric systems, in which  
2 PMN-PT (27.1  $\%/(kVmm^{-1})$ ), PNN-PZT (26  $\%/(kVmm^{-1})$ ), and PMN-PNN-PT (23.8  
3  $\%/(kVmm^{-1})$ ) exhibit larger values but PNN-PT (13.1  $\%/(kVmm^{-1})$ ) a smaller one. We  
4 can find a direct correlation between the rate of polarization rotation  $d\theta/dE$  and the  
5 macroscopic measured piezoelectric coefficient  $d_{33}$  [Fig. 2(b)]. The higher rate of  
6 polarization rotation conforms to a high piezoelectric coefficient  $d_{33}$ . A large value of  
7  $d\theta/dE$  empowers a small electric field to drive a large change of polarization vector  
8 angle. This critical role of polarization rotation can also be supported by the  
9 phenomenon that the electric field necessary for polarization rotation decreases  
10 significantly when approaching the critical point where the piezoelectric performance  
11 is maximum such as in the PMN-PT single crystals [11]. This is in accordance with  
12 Landau-Ginsburg-Devonshire (LGD) phenomenological theory as facilitated  
13 polarization rotation manifests large dielectric susceptibility, and therefore gives rise  
14 to large piezoelectric response [23].

15 Piezoelectric response is generally contributed from the intrinsic lattice strain and  
16 extrinsic domain switching effects. Since the present four piezoelectric systems  
17 exhibit a single monoclinic structure, the extrinsic domain switching and the intrinsic  
18 lattice strain contributions can be extracted from the  $\{002\}_{PC}$  profile at the  $0^\circ$  sector,  
19 which was fitted by two peaks using Pseudo-Voigt function [18]. The changes of  
20 integrated intensities of the reflections can be correlated to the domain switching  
21 ( $\eta_{norm}$ ).  $\eta_{norm}$  indicates the normalized relative volume fraction of switched domains,  
22 which is suitable for comparison among different symmetries. The position shift of  
23 the reflections can be utilized for evaluating the lattice strain ( $\epsilon$ ) [18,37-41]. The

1 electric field dependence of  $\eta_{\text{norm}}$  is plotted in Fig. S11(a) of Ref. [26]. Firstly, it is  
2 interesting to find that the monoclinic phase exhibits a very large domain  
3 rearrangement fraction by electric poling. The value of  $\eta_{\text{norm}}$  is above 70% for the four  
4 piezoelectric systems after the release of electric field, which is much higher than that  
5 of T and R phases [37, 38]. A large value of  $\eta_{\text{norm}}$  was also observed in the monoclinic  
6  $\text{PbZr}_{0.535}\text{Ti}_{0.465}\text{O}_3$  ceramic [18]. It strongly supports the notion that the non-180°  
7 domains of the monoclinic phase are much easier aligned to electric field direction as  
8 compared to the tetragonal and rhombohedral ones [42]. Secondly, monoclinic phase  
9 exhibits negligible domain switching after electric poling. To quantitatively estimate  
10 the domain switching of monoclinic phase as function of electric field, the ratio of  
11  $\Delta\eta_{\text{norm}}/\Delta E$  was calculated. It is as small as 0.43%/(kVcm<sup>-1</sup>), 0.67%/(kVcm<sup>-1</sup>),  
12 0.19%/(kVcm<sup>-1</sup>), 1.15%/(kVcm<sup>-1</sup>) for the monoclinic phase in the PMN-PT,  
13 PNN-PZT, PMN-PNN-PT, PNN-PT, respectively. This implies that the monoclinic  
14 phase exhibits a common behavior of negligible domain switching, when compared  
15 with those of T and R phases [18,39,40]. Thus, the piezoelectric response of the  
16 monoclinic phase must originate from the intrinsic contribution of lattice strain.

17 The electric field dependence of lattice strain is provided in Fig. S11(b) of Ref.  
18 [26]. The (200)<sub>PC</sub> strain reveals a linear relationship with electric field, in which the  
19 slope indicates the piezoelectric coefficient  $d_{33}^*$  of intrinsic lattice strain. PMN-PT,  
20 PNN-PZT, PMN-PNN-PT and PNN-PT exhibit 982 pm/V, 854 pm/V, 684 pm/V, and  
21 564 pm/V, respectively. Similarly,  $d_{33}^*$  is also correlated with  $d\theta/dE$  [Fig. 2(c)]. The  
22 present results lead to the conclusion that the monoclinic phase exhibits common  
23 piezoelectric properties of negligible domain switching and large lattice strain.



1

2 FIG. 3. (a) The relationship between the macroscopic measured  $d_{33}$  and phase  
 3 structure. The other  $d_{33}$  values of PT-100xBS ( $(1-x)\text{PbTiO}_3-x\text{BiScO}_3$ ), PT-60BMT  
 4 ( $0.4\text{PbTiO}_3-0.6\text{BiMg}_{1/2}\text{Ti}_{1/2}\text{O}_3$ ), PT-47BNT ( $0.53\text{PbTiO}_3-0.47\text{BiNi}_{1/2}\text{Ti}_{1/2}\text{O}_3$ ) and La  
 5 doped  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  (PLZT100x) are adopted from the literature [39, 43-45]. (b)  
 6 Schematic illustration of monoclinic polarization vectors at zero electric field in the  
 7  $(110)_{PC}$  plane. The boundary between  $M_A$  and  $M_B$  is indicated by the dashed line. (c)  
 8 Schematic illustration of the coupling between electric-field-driven-polarization  
 9 rotation and intrinsic lattice strain.

10 As presented in Fig. 2 (b) and (c), the critical role of monoclinic polarization  
 11 rotation for the high-performance of piezoelectrics has been corroborated. Here we  
 12 emphasize the fundamental relationship between the piezoelectric property and crystal  
 13 structure for lead-based perovskites [Fig. 3(a)]. Importantly, the  $M_A$  phase  
 14 corresponds to the highest piezoelectric performance, while the other crystal

1 structures of  $M_B$ , R and T yield more or less inferior piezoelectric performance. The  
2 polarization vectors of monoclinic phase under zero electric field are highlighted as an  
3 example in Fig. 3(b). For the  $M_A$  structure, the polarization can rotate from the  
4 direction between  $[001]_{PC}$  and  $[111]_{PC}$ , with a larger range of  $\theta$  variation ( $54.7^\circ$ ).  
5 However, for the  $M_B$  structure the polarization rotates between  $[111]_{PC}$  and  $[110]_{PC}$   
6 with a smaller range of  $\theta$  variation ( $35.3^\circ$ ). The piezoelectric response is strongly  
7 coupled to polarization variation. The extension of the polarization component is  
8 connected to the intrinsic lattice strain when the polarization rotation is driven by the  
9 electric field [Fig. 3(c)]. The origin of the enhancement of piezoelectric activity has  
10 been widely demonstrated by the LGD thermodynamic theory calculation in the T, R,  
11 and O phase in the MPB region [14,23,46,47]. It is believed that the  $M_A$  structure  
12 would be more beneficial to polarization rotation than the  $M_B$  structure due to the  
13 flatter free energy profile [14]. The low contribution by the anisotropic free energy  
14 indicates enhanced susceptibility of the atomic displacements, resulting in giant  
15 piezoelectric performance [23,47]. Therefore, it is much easier to achieve higher  
16 performance of piezoelectrics in the  $M_A$  structure. Also in the previous first-principle  
17 calculation for the single crystal  $BaTiO_3$  the piezoelectric responses of the  $M_A$  path is  
18 5 times larger than that of the  $M_B$  path [14].

19 Additionally, much inferior piezoelectric property of the T and R phases is due to  
20 fewer available polarization directions. There are only 8 for rhombohedral and 6  
21 directions for tetragonal phase in comparison to the monoclinic phase (24 polarization  
22 directions). In the perovskite ferroelectrics, the crystallographic symmetry has a  
23 strong influence on ferroelectric domain switching [42]. Compared to the advantage

1 of the continuous rotation of polarization in the monoclinic phase, the polarization  
2 vector is fixed in one of the directions of  $[001]_{PC}$  for the T phase and  $[111]_{PC}$  for the R  
3 phase. The polarization of T and R phases is not allowed to smoothly rotate under the  
4 electric field. Thus much inferior piezoelectric property is generated.

5 The present understanding of the piezoelectric mechanism will be helpful for the  
6 design of high-performance perovskite piezoelectric materials in the future. It is  
7 pertinent to obtain the crystal structure which enables polarization rotation smoothly  
8 driven by electric field in order to obtain a piezoelectric with higher performance.

9 In summary, a single electric field-induced monoclinic phase has been identified in  
10 compositions of all four systems of PMN-PT, PNN-PZT, PMN-PNN-PT and PNN-PT.  
11 A visualized polarization rotation within the  $(110)_{PC}$  plane of the monoclinic phase  
12 driven by electric field has been observed. In perovskite ferroelectrics, a direct  
13 correlation between structure and piezoelectric property has been established.  
14 Monoclinic  $M_A$  phase indicates a superior piezoelectric property and other structures  
15 such as  $M_B$ , R, T exhibit inferior property. The piezoelectric property depends  
16 critically on the sensitivity of polarization rotation to electric field. A strong tendency  
17 of electric-field-driven polarization rotation generates peak piezoelectric performance.  
18 It is mainly attributed to intrinsic lattice strain and little to extrinsic domain wall  
19 motion. The present results reveal that the sensitivity of polarization rotation plays a  
20 key role in the design of new high-performance piezoelectric materials in the future.

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