University of Wollongong

Research Online

Australian Institute for Innovative Materials -
Papers

Australian Institute for Innovative Materials

1-1-2014

PMN-PT based quaternary piezoceramics with enhanced piezoelectricity and temperature stability

Nengneng Luo
Tsinghua University

Shujun Zhang
Pennsylvania State University, shujun@uow.edu.au

Qiang Li
Tsinghua University

Qingfeng Yan
Tsinghua University

Wenhui He
Tsinghua University

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/aiimpapers>

Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

PMN-PT based quaternary piezoceramics with enhanced piezoelectricity and temperature stability

Abstract

The phase structure, piezoelectric, dielectric, and ferroelectric properties of (0.80-x)PMN-0.10PFN-0.10PZ-xPT were investigated systematically. The morphotropic phase boundary (MPB) was confirmed to be 0.30

Keywords

piezoelectricity, enhanced, stability, piezoceramics, temperature, quaternary, pt, pmn

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Luo, N., Zhang, S., Li, Q., Yan, Q., He, W., Zhang, Y. & Shrout, T. R. (2014). PMN-PT based quaternary piezoceramics with enhanced piezoelectricity and temperature stability. *Applied Physics Letters*, 104 (18), 182911-1-182911-5.

Authors

Nengneng Luo, Shujun Zhang, Qiang Li, Qingfeng Yan, Wenhui He, Yiling Zhang, and Thomas R. Shrout

PMN-PT based quaternary piezoceramics with enhanced piezoelectricity and temperature stability

Nengneng Luo, Shujun Zhang, Qiang Li, Qingfeng Yan, Wenhui He, Yiling Zhang, and Thomas R Shrout

Citation: [Applied Physics Letters](#) **104**, 182911 (2014); doi: 10.1063/1.4875797

View online: <http://dx.doi.org/10.1063/1.4875797>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/104/18?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Enhanced dielectric, ferroelectric, and electrostrictive properties of \$\text{Pb}\(\text{Mg}_{1/3}\text{Nb}_{2/3}\)_{0.9}\text{Ti}_{0.1}\text{O}_3\$ ceramics by ZnO modification](#)

[J. Appl. Phys.](#) **113**, 204101 (2013); 10.1063/1.4801881

[The study of dielectric, pyroelectric and piezoelectric properties on hot pressed PZT-PMN systems](#)

[AIP Advances](#) **2**, 042170 (2012); 10.1063/1.4769889

[Structure, piezoelectric, and ferroelectric properties of \$\text{BaZrO}_3\$ substituted \$\text{Bi}\(\text{Mg}_{1/2}\text{Ti}_{1/2}\)\text{O}_3\$ - \$\text{PbTiO}_3\$ perovskite](#)

[J. Appl. Phys.](#) **111**, 104118 (2012); 10.1063/1.4722286

[Piezoelectric properties and temperature stability of Mn-doped \$\text{Pb}\(\text{Mg}_{1/3}\text{Nb}_{2/3}\)\$ - \$\text{PbZrO}_3\$ - \$\text{PbTiO}_3\$ textured ceramics](#)

[Appl. Phys. Lett.](#) **100**, 132908 (2012); 10.1063/1.3698157

[High temperature properties of \$\text{BiScO}_3\$ – \$\text{PbTiO}_3\$ piezoelectric ceramics](#)

[J. Appl. Phys.](#) **106**, 014102 (2009); 10.1063/1.3158542

Launching in 2016!
The future of applied photonics research is here

AIP | APL
Photonics

PMN-PT based quaternary piezoceramics with enhanced piezoelectricity and temperature stability

Nengneng Luo,^{1,2} Shujun Zhang,² Qiang Li,^{1,a)} Qingfeng Yan,¹ Wenhui He,¹ Yiling Zhang,³ and Thomas R Shrout²

¹Department of Chemistry, Tsinghua University, Beijing 100084, China

²Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802, USA

³School of Materials Science & Engineering, Tsinghua University, Beijing 100084, China

(Received 5 March 2014; accepted 28 April 2014; published online 9 May 2014)

The phase structure, piezoelectric, dielectric, and ferroelectric properties of $(0.80 - x)\text{PMN}-0.10\text{PFN}-0.10\text{PZ}-x\text{PT}$ were investigated systematically. The morphotropic phase boundary (MPB) was confirmed to be $0.30 < x < 0.34$. Both MPB compositions of $x = 0.32$ and $x = 0.33$ exhibit high piezoelectric coefficients $d_{33} = 640$ pC/N and 580 pC/N, electromechanical couplings k_p of 0.53 and 0.52, respectively. Of particular importance is that the composition with $x = 0.33$ was found to process high field-induced piezoelectric strain coefficient d_{33}^* of 680 pm/V, exhibiting a minimal temperature-dependent behavior, being less than 8% in the temperature range of 25–165 °C, which can be further confirmed by d_{31} , with a variation of less than 9%. The temperature-insensitive d_{33}^* values can be explained by the counterbalance of the ascending dielectric permittivity and descending polarization with increasing temperature. These features make the PMN-PT based quaternary MPB compositions promising for actuator applications demanding high temperature stability. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4875797>]

Lead-based relaxor ferroelectric materials with perovskite structure have been actively investigated since 1970s due to their good electromechanical properties, among which, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) was reported to process extra high electromechanical coupling factor and piezoelectric coefficient, making it one of the most promising candidates for piezoelectric actuator, sensor, and transducer applications.^{1–3} Generally, the enhanced electromechanical properties can be obtained at morphotropic phase boundary (MPB) region.^{4,5} However, the applications of the PMN-PT ferroelectric materials with MPB compositions are limited by the loss of temperature stability, because of the relatively low Curie temperature ($T_c \sim 130\text{--}170^\circ\text{C}$) and much lower rhombohedral to tetragonal ferroelectric phase transition temperature ($T_{rt} \sim 50\text{--}85^\circ\text{C}$) due to the strongly curved MPB. Therefore, over the past few years, tremendous efforts have been made to improve the temperature stability of the properties, two potential approaches have been adopted so far: shifting T_c/T_{rt} to higher temperature by composition tuning, and taking advantage of the engineered domain configuration in single crystals.³ In the first method, through elements substituting and/or adding of other end-members, numerous new higher T_c/T_{rt} binary and ternary material systems were developed, including $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{-PbTiO}_3$ (PIN-PT),^{6,7} $\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{-PbTiO}_3$ (PYN-PT),^{8,9} $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{-PbTiO}_3$ (PSN-PT),¹⁰ $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT),^{11–15} $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbZrO}_3\text{-PbTiO}_3$ (PMN-PZ-PT),^{16–19} and $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PSN-PMN-PT),²⁰ etc. However, it was found that the temperature stability remained unsolved despite of the high T_c/T_{rt} . Take PIN-PMN-PT ceramics for example, the variation of d_{33}

was reported to be $\sim 20\%$ at 150°C when compared with that at room temperature.¹³ It was expected that the $\text{Bi}(\text{Me})\text{O}_3\text{-PbTiO}_3$ compositions with higher $T_c > 300^\circ\text{C}$ will shed light on the potentiality of achieving high temperature stability.^{21–26} However, except $\text{BiScO}_3\text{-PbTiO}_3$ (BS-PT),²¹ the piezoelectric coefficients of the reported $\text{Bi}(\text{Me})\text{O}_3\text{-PbTiO}_3$ based ceramics, such as $\text{BiFeO}_3\text{-PbTiO}_3$ (BF-PT),²² $\text{BiInO}_3\text{-PbTiO}_3$ (BI-PT),²³ $\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-PbTiO}_3$ (BNT-PT),²⁴ $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-PbTiO}_3$ (BMT-PT),^{25,26} etc., were lower than 300 pC/N at their respective MPBs. Furthermore, it was reported that piezoelectric coefficients exhibited different degree of degradation in binary and ternary systems, not necessarily associated with their T_c/T_{rt} , though higher T_c indicating broader usage temperature range.²⁷ In the second method, investigations were focused on preparing single crystals with engineered domain configurations, where greatly enhanced piezoelectric d_{33} was obtained taking advantage of the crystallographic anisotropy. Nevertheless, the longitudinal piezoelectric coefficient d_{33} still exhibited large temperature-dependent variation when MPB compositions were selected.^{9,12,14,17,18,28} Of particular significance is that the thickness shear piezoelectric d_{24} in [011]-poled orthorhombic relaxor- PbTiO_3 crystals was reported to possess excellent temperature stability with high value being on the order of ~ 2100 pC/N, due to the vertical R-O MPB.^{15,29} However, the complex synthesis or growth method is too expensive to enable mass production and commercialization. As a result, the development of high performance piezoelectric materials is still hampered due to the insufficient temperature stability.

For polycrystalline ceramics, a multiple end-members system may help adjusting the properties of materials more efficiently, taking advantage of each end-member. It was noted that most PMN-PT based ternary systems generally exhibited improved comprehensive performance when compared with that of binary systems, such as higher T_{rt} with comparable

^{a)}Author to whom correspondence should be addressed. Electronic mail: qiangli@mails.tsinghua.edu.cn. Tel.: +86-10-62797871. Fax: +86-10-62771149.

FIG. 1. XRD patterns of the as-sintered PMN-PFN-PZ-PT ceramics. (a) $2\theta = 15^\circ\text{--}70^\circ$, (b) (200)-reflections at $2\theta = 44^\circ\text{--}46^\circ$.

piezoelectric properties.^{11–20,30} The PMN-PZ-PT ternary system, which can be regarded as the combination of PMN-PT and PZT, was reported to possess high ferroelectric phase transition temperatures and high coercive fields, the as-grown PMN-PZ-PT single crystals were considered to be the second generation relaxor-PT crystals.³ $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) is a typical relaxor ferroelectric material with high dielectric permittivity. Through the hybridization of PMN-PT, PZT, and PFN, a quaternary system $(0.85-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}0.10\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{--}0.05\text{PbZrO}_3\text{--}x\text{PbTiO}_3$ (PMN-PFN-PZ-PT) was reported with high $d_{33} > 600$ pC/N and enhanced ferroelectric phase transition temperature.³¹

In this work, by tuning the amount of PZ end-member, a quaternary system $(0.80-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}0.10\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{--}0.10\text{PbZrO}_3\text{--}x\text{PbTiO}_3$ at MPB region was explored, which exhibited enhanced piezoelectricity and high temperature stability from room temperature to 165°C . The mechanism of temperature stable piezoelectric response was explained, pioneering new approach of developing temperature-insensitive piezoelectric actuators.

$(0.80-x)\text{PMN}\text{--}0.10\text{PFN}\text{--}0.10\text{PZ}\text{--}x\text{PT}$ ceramics with $x = 0.30\text{--}0.34$ were prepared by conventional solid state reaction, following the procedure reported earlier.³¹ Disk and bar samples with electrodes on the large faces were prepared for the electric properties measurement, as described in the IEEE Standards.³² The crystal structure of the as-sintered samples was determined using an X-ray diffractometer (D8 ADVANCE, Brüker, German) with Cu K_α radiation at 2θ from 15° to 70° . The temperature dependence of dielectric properties were measured at 1 kHz using an Agilent 4294A (Agilent Inc., Bayan, Malaysia) impedance analyzer connected to a Delta 9023 (Delta Design Inc., San Diego, America) temperature control system. All samples were poled under 3 kV/mm DC field at 120°C for 15 min in silicon oil. Room temperature piezoelectric coefficient d_{33} of disk samples were measured using a quasi-static piezo- d_{33} meter (ZJ-4A, Institute of Acoustics, Chinese Academy of Sciences, China). The temperature dependence of hysteresis loop (P - E) and unipolar strain (S_{uni} - E) were measured at

1 Hz using a ferroelectric tester (TF2000, aixACCT, Aachen, Germany). The values of k_p and k_t , k_{31} and d_{31} were determined using disk and bar samples, respectively, by the resonant-antiresonant method. The value of k_{33} was estimated by k_p and k_t using the following equation:³³

$$(k_{33})^2 \approx (k_p)^2 + (k_t)^2 - (k_p)^2(k_t)^2. \quad (1)$$

The room temperature XRD patterns of all as-sintered PMN-PFN-PZ-PT ceramics are shown in Fig. 1(b). All peaks can be identified to the corresponding Miller indices, which indicate the as-sintered ceramics are of pure perovskite structure. Fig. 1(b) gives the enlarged (200)-reflections in the range of $2\theta = 44^\circ\text{--}46^\circ$, which are fitted using the Lorentzian function. The (200)-reflection changes obviously with increasing PT content. When $x = 0.30$, only a single $(200)_R$ -peak is observed, indicating a rhombohedral (R) phase; at $x = 0.34$, the (200)-peak splits into two peaks $(200)_T$ and $(002)_T$, demonstrating a tetragonal (T) phase; while for the compositions in the range of $0.30 < x < 0.34$, the peaks are very broad and can be fitted by three peaks: $(002)_T$, $(200)_R$, and $(200)_T$, indicating a mixture of rhombohedral and tetragonal phases. Therefore, the MPB region can be determined at $0.30 < x < 0.34$.

Figs. 2(a) and 2(b) reveal the composition dependence of piezoelectric, dielectric, and ferroelectric properties of as-explored quaternary system at room temperature. Well-saturated hysteresis loops were obtained at 30 kV/cm in Fig. 2(a). From Figs. 2(b1)–2(b3), it can be found that the highest piezoelectric coefficient d_{33} , planar electromechanical coupling k_p and dielectric permittivity ϵ_r appear at MPB region determined by XRD analysis. The highest d_{33} and k_p were found to be 640 pC/N, 0.53 at $x = 0.32$, while the composition on the tetragonal side of MPB ($x = 0.33$) has the highest ϵ_r of 2630 and high d_{33} of 580 pC/N. Fig. 2(b4) gives the field-induced piezoelectric strain coefficient $d_{33}^* = S_{\text{max}}/E_{\text{max}}$ (S_{max} is the maximum strain and E_{max} is the maximum electric field, ~ 10 kV/cm in this study) calculated from the data in Fig. 2(c), which exhibits a similar composition-dependent tendency with the d_{33} measured by quasi-static piezo- d_{33}

FIG. 2. (a) Hysteresis loops of $x = 0.30$, $x = 0.32$, and $x = 0.34$. (b1) Piezoelectric coefficients d_{33} , (b2) planar electromechanical coupling k_p , (b3) dielectric permittivity ϵ_r , (b4) field-induced piezoelectric strain coefficient d_{33}^* , (b5) remnant polarization P_r , (b6) coercive field E_c . (c) Unipolar $S_{\text{uni}}-E$ curves at room temperature. (d) Temperature dependence of dielectric permittivity ϵ_r and $\tan \delta$ of poled samples. (e) Temperature-composition phase diagram of PMN-PFN-PZ-PT quaternary system.

meter. The samples with MPB composition exhibit large piezoelectric coefficient d_{33}^* of 620 pm/V, 700 pm/V, and 680 pm/V for $x = 0.31$, $x = 0.32$, and $x = 0.33$, respectively. The remnant polarization P_r are almost stable in the order of $25 \mu\text{C}/\text{cm}^2$ for both R phase and MPB compositions, while an abrupt decrease of $P_r = 20 \mu\text{C}/\text{cm}^2$ is observed for T phase composition at $x = 0.34$. This phenomenon can be explained by the more equivalent directions of domain states in R/MPB phase and the clamping of domain wall in T phase.³⁴ Fig. 2(b6) shows that the coercive field E_c increases with increasing PT content, ranging from 6.4 to 9.4 kV/cm, attributing to the increased tetragonal component.

The temperature dependence of dielectric permittivity ϵ_r and $\tan \delta$ at 1 kHz with various PT contents are presented in Fig. 2(d). The dielectric losses of all compositions are around 0.015 at room temperature. Two dielectric anomalies can be observed for R-rich samples, being related to the rhombohedral-tetragonal ferroelectric phase transition temperature T_{rt} and ferroelectric-paraelectric phase transition temperature T_c , respectively. Of particular significance is that the dielectric permittivity exhibits an improved temperature stability with increasing PT content, and there is no ferroelectric phase transition being observed prior to Curie temperature for MPB composition $x = 0.33$. Based on the results of temperature-dependent dielectric permittivity, an isothermal phase diagram of PMN-PFN-PZ-PT system is established and plotted as a function of PT content, as shown in Fig. 2(e). It is evident that T_c enhances linearly from 195 °C to 217 °C with

increasing PT content, due to the high $T_c \approx 490$ °C of PT. The rhombohedral-tetragonal phase transition temperature T_{rt} decreases and finally disappears when the phase structure transforms from rhombohedral-rich phase to tetragonal-rich phase. An enhancement of T_{rt} about 30 °C is achieved for the quaternary system, when compared with that of PMN-PT counterpart, rising from 84 °C to about 116 °C. Compared with the previously reported PMN-PFN-PZ-PT system with 5% PZ,³¹ the compositions with 10% PZ at MPB process comparable piezoelectric coefficient and electromechanical coupling, but higher T_c/T_{rt} , indicating a broader usage temperature range.

To evaluate the thermal stability performance, the unipolar strains $S_{\text{uni}}-E$ were measured as a function of temperature. Fig. 3(a) is an example of the temperature-dependent unipolar strain for $x = 0.33$ measured at 10 kV/cm, in which typical linear $S_{\text{uni}}-E$ curves can be observed. The d_{33}^* values derived from the unipolar strains of all compositions are plotted in Fig. 3(b). For samples with lower PT content, d_{33}^* is found to increase quickly with increasing temperature, reaching maximum value at their corresponding T_{rt} . With increasing PT content, the variation of d_{33}^* becomes smaller and the inverse temperature decreases from 115 °C for $x = 0.30$ to below room temperature when $x \geq 0.34$. Of particular interest is that high d_{33}^* value with a minimal temperature-dependent variation is obtained for $x = 0.33$, in the temperature range of 25–165 °C. Fig. 3(c) shows the normalized piezoelectric value $d_{33}^*_{\text{T}}/d_{33}^*_{\text{RT}}$ as a function of temperature for different ceramic systems. It should be noted

FIG. 3. (a) Temperature-dependent unipolar strain for $x=0.33$. (b) Temperature dependence of d_{33}^* for ceramics with different PT contents. (c) Comparison of temperature dependence of piezoelectric coefficients for various piezoceramics as normalized to their room temperature values d_{33}^*/d_{33}^{RT} . The data for PZT5H,³⁵ PZT4,³⁶ BMN-PT,²⁵ BS-PT,²⁶ NKL-NT-CZ,³⁷ and BZT-50BCT³⁸ are derived from figures in the respective references. The piezoelectric coefficient of BZT-50BCT measured by a commercial Berlingcourt-type d_{33} meter. (d) Temperature dependences of $k_p, k_t, k_{33}, k_{31},$ and d_{31} normalized to their room temperature values for $x=0.33$.

that the variation of d_{33}^* for PMN-PFN-PZ-PT ceramics with $x=0.33$ is less than 8% in the investigated temperature range, much lower than those of commercial PZT5H (>20%)³⁵ and PZT4 (~15%)³⁶ ceramics, and outperforms slightly compared with BMT-PT²⁵ and BST-PT²⁶ which possess much higher Curie temperature of >300 °C. In addition, $(\text{Na}_{0.49}\text{K}_{0.49}\text{Li}_{0.02})(\text{Nb}_{0.8}\text{Ta}_{0.2})\text{O}_3\text{-}0.05\text{CaZrO}_3$ (NKL-NT-CZ)³⁷ lead-free ceramics exhibit a comparable d_{33}^* variation of ~10% in the studied temperature range, however, the value of d_{33}^* is 320 pm/V, being only half of that of $x=0.33$; while $\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3\text{-}50(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (BZT-50BCT)³⁸ has much lower Curie temperature and its d_{33} decreases to nearly 60% of the room temperature value when temperature increases to 70 °C. The high field-induced piezoelectric strain coefficient and excellent temperature stability of $x=0.33$ make it promising for temperature-insensitive actuator devices.

To further evaluate the temperature stability of $x=0.33$, the value of $k_p, k_t, k_{33}, k_{31},$ and d_{31} were calculated/estimated as a function of temperature. As shown in Fig. 3(d), $k_p, k_t, k_{33},$ and k_{31} decrease with increasing temperature, with a reduction ranging from 10% to 20%. While the d_{31} exhibits high temperature stability with a variation of less than 9%, similar to that of piezoelectric coefficient d_{33}^* , which further confirms that $x=0.33$ processes high temperature stability of piezoelectric properties.

The results provide strong evidence that high temperature stability of piezoelectric coefficient can be achieved for $x=0.33$, which can be explained by the phenomenological relationship of electrostriction in ferroelectrics. Generally, electrostrictive coefficient Q , dielectric permittivity ϵ_r , and polarization P contribute to d_{33}^* , following the equation:³⁹

$$d_{33}^* \propto Q\epsilon_0\epsilon_r P, \quad (2)$$

where ϵ_0 is vacuum permittivity. P approximately equals to the remnant polarization P_r for ferroelectric ceramics. The electrostrictive Q is insensitive to temperature, ferroelectric phase structure, and phase transition in perovskite materials when compared with the strong temperature dependent dielectric properties.⁴⁰ The equation above suggests that the variation of d_{33}^* is mainly related to $\epsilon_r \times P$. The temperature-dependent maximum polarization $P_{\max}$, remnant polarization P_r , coercive field E_c , and dielectric permittivity ϵ_r for $x=0.30$ and $x=0.33$ are given in Figs. 4(a) and 4(b), respectively. $P_{\max}$ and P_r decrease monotonically with increasing temperature, resulting from the so-called pyroelectric effect,⁴¹ and E_c exhibits the same trend, due to the easier domain wall motion at elevated temperature. On the contrary, ϵ_r increases with increasing temperature for both compositions. An abrupt enhancement of ϵ_r near the ferroelectric phase transition temperature can be found for $x=0.30$; while ϵ_r is much flatter for $x=0.33$, due to the smeared free energy barrier between rhombohedral and tetragonal phases. The value of $\epsilon_r \times P$ for $x=0.30$ is found to increase with increasing temperature, with inversion point occurring around 115 °C, due to the ferroelectric phase transition, which is consistent with the evolution of d_{33}^* , as depicted in Fig. 4(a). Of particular importance is that the value of $\epsilon_r \times P$ for $x=0.33$ is nearly temperature-independent from 25 °C to 165 °C, as shown in Fig. 4(b), accounting for the high temperature stability of d_{33}^* . From the phenomenological descriptions above, it can be concluded that the origin of temperature-insensitive field-induced d_{33}^* may result from the counterbalance of the ascending dielectric permittivity and descending polarization with increasing temperature. Thus, if the dielectric permittivity anomaly near the ferroelectric phase transition temperature for MPB compositions is shifted or smeared by composition tuning, to achieve a stable value of $\epsilon_r \times P$, a temperature-insensitive d_{33}^* can be expected, this is the case

FIG. 4. Temperature dependence of various parameters, χ_T/χ_{RT} stands for $P_{\max}$, P_r , E_c , d_{33}^* , ε_r and $\varepsilon_r \times P_r$ for (a) $x=0.30$ and (b) $x=0.33$, respectively.

for $x=0.33$. Otherwise, a d_{33}^* peak will exist at the phase transition temperature, which is the phenomenon of $x=0.30$.

In summary, PMN-PFN-PZ-PT ceramics with compositions near MPB were prepared, which exhibit high piezoelectric coefficient near MPB, with $d_{33}=640$ pC/N and 580 pC/N at $x=0.32$ and $x=0.33$, respectively. Of particular importance is that the composition of $x=0.33$ exhibited high field-induced piezoelectric strain coefficient d_{33}^* of 680 pm/V, with a minimal temperature-dependent variation being on the order of $<8\%$ in the temperature range of 25–165 °C which is further confirmed by d_{31} , making it promising for actuator applications demanding good temperature stability. It is supposed that by shifting or smearing the dielectric permittivity anomaly near the ferroelectric phase transition temperature for MPB compositions through composition tuning, a temperature-insensitive d_{33}^* can be expected, according to Eq. (1).

The authors from Tsinghua University acknowledge the National Basic Research Program of China (Grant No. 2013CB632900), the National Natural Science Foundation of China (Nos. 50972071 and 51172118), Tsinghua University Initiative Scientific Research Program (Grant No. 20131089218), and the funds of State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China. The author (Nengneng Luo) wishes

to acknowledge the support from the China Scholarship Council.

- ¹S. E. Park and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).
- ²G. Liu, W. H. Jiang, J. Q. Zhu, and W. W. Cao, *Appl. Phys. Lett.* **99**, 162901 (2011).
- ³S. J. Zhang and F. Li, *J. Appl. Phys.* **111**, 031301 (2012).
- ⁴L. E. Cross, *Ferroelectrics* **76**, 241 (1987).
- ⁵Z. Y. Feng, X. Y. Zhao, and H. S. Luo, *J. Appl. Phys.* **100**, 024104 (2006).
- ⁶C. Augier, M. PhamThi, H. Dammak, and P. Gaucher, *J. Eur. Ceram. Soc.* **25**, 2429 (2005).
- ⁷N. Yasuda, H. Ohwa, M. Kume, K. Hayashi, Y. Hosono, and Y. Yamashita, *J. Cryst. Growth* **229**, 299 (2001).
- ⁸N. Yasuda, H. Ohwa, M. Kume, Y. Hosono, Y. Yamashita, S. Ishino, H. Terauchi, M. Iwata, and Y. Ishibashi, *Jpn. J. Appl. Phys., Part 1* **40**, 5664 (2001).
- ⁹S. J. Zhang, L. Lebrun, S. Rhee, C. Randall, and T. R. Shrout, *Appl. Phys. Lett.* **81**, 892 (2002).
- ¹⁰Y. Yamashita, *Jpn. J. Appl. Phys., Part 1* **33**, 4652 (1994).
- ¹¹Y. Hosono, Y. Yamashita, H. Sakamoto, and N. Ichinose, *Jpn. J. Appl. Phys., Part 1* **41**, L1240 (2002).
- ¹²G. S. Xu, K. Chen, D. F. Yang, and J. B. Li, *Appl. Phys. Lett.* **90**, 032901 (2007).
- ¹³D. B. Lin, Z. R. Li, F. Li, Z. Xu, and X. Yao, *J. Alloys Compd.* **489**, 115 (2010).
- ¹⁴F. Li, S. J. Zhang, Z. Xu, X. Y. Wei, J. Luo, and T. R. Shrout, *J. Am. Ceram. Soc.* **93**, 2731 (2010).
- ¹⁵F. Li, S. J. Zhang, Z. Xu, X. Y. Wei, J. Luo, X. Y. Wei, and T. R. Shrout, *Appl. Phys. Lett.* **97**, 252903 (2010).
- ¹⁶Z. G. Xia and Q. Li, *J. Phys. D: Appl. Phys.* **40**, 7826 (2007).
- ¹⁷S. J. Zhang, S. M. Lee, D. H. Kim, H. Y. Lee, and T. R. Shrout, *Appl. Phys. Lett.* **90**, 232911 (2007).
- ¹⁸Z. G. Xia, Q. Li, and S. F. Zhang, *Solid State Commun.* **145**, 38 (2008).
- ¹⁹S. J. Zhang, S. M. Lee, D. H. Kim, H. Y. Lee, and T. R. Shrout, *Appl. Phys. Lett.* **93**, 122908 (2008).
- ²⁰Y. Hosono, K. Harada, Y. Yamashita, M. Dong, and Z. G. Ye, *Jpn. J. Appl. Phys., Part 1* **39**, 5589 (2000).
- ²¹R. E. Eitel, C. A. Randall, T. R. Shrout, P. W. Rehrig, W. Hackenberger, and S. E. Park, *Jpn. J. Appl. Phys., Part 1* **40**, 5999 (2001).
- ²²T. P. Comyn, S. P. McBride, and A. J. Bell, *Mater. Lett.* **58**, 3844 (2004).
- ²³S. J. Zhang, R. Xia, C. A. Randall, and T. R. Shrout, *J. Mater. Res.* **20**, 2067 (2005).
- ²⁴S. M. Choi, C. J. Stringer, T. R. Shrout, and C. A. Randall, *J. Appl. Phys.* **98**, 034108 (2005).
- ²⁵Q. Zhang, Z. R. Li, F. Li, Z. Xu, and X. Yao, *J. Am. Ceram. Soc.* **93**, 3330 (2010).
- ²⁶T. Leist, J. Chen, W. Jo, E. Aulbach, J. Suffner, and J. Rödel, *J. Am. Ceram. Soc.* **95**, 711 (2012).
- ²⁷S. J. Zhang and T. R. Shrout, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **57**, 2138 (2010).
- ²⁸J. Tian, P. D. Han, X. L. Huang, H. X. Pan, J. F. Carroll III, and D. A. Payne, *Appl. Phys. Lett.* **91**, 222903 (2007).
- ²⁹F. Li, S. J. Zhang, Z. Xu, X. Y. Wei, and T. R. Shrout, *Adv. Funct. Mater.* **21**, 2118 (2011).
- ³⁰N. N. Luo, Y. Y. Li, Z. G. Xia, and Q. Li, *CrystEngComm* **14**, 4547 (2012).
- ³¹N. N. Luo, Q. Li, Z. G. Xia, and X. C. Chu, *J. Am. Ceram. Soc.* **95**, 3246 (2012).
- ³²IEEE Standards on Piezoelectricity, ANSI/IEEE Standard, New York (1987).
- ³³S. J. Zhang, E. F. Alberta, R. E. Eitel, C. A. Randall, and T. R. Shrout, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **52**, 2131 (2005).
- ³⁴L. Jin, F. Li, and S. J. Zhang, *J. Am. Ceram. Soc.* **97**, 1 (2014).
- ³⁵D. Wang, Y. Fotinich, and G. P. Carman, *J. Appl. Phys.* **83**, 5342 (1998).
- ³⁶Y. Sait, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, *Nature* **432**, 84 (2004).
- ³⁷K. Wang, F. Z. Yao, W. Jo, D. Gobeljic, V. V. Shvartsman, D. C. Lupascu, J. F. Li, and J. Rödel, *Adv. Funct. Mater.* **23**, 4079 (2013).
- ³⁸W. F. Liu and X. B. Ren, *Phys. Rev. Lett.* **103**, 257602 (2009).
- ³⁹J. Kuwata, K. Uchino, and S. Nomura, *Jpn. J. Appl. Phys., Part 1* **19**, 2099 (1980).
- ⁴⁰F. Li, L. Jin, Z. Xu, and S. J. Zhang, *Appl. Phys. Rev.* **1**, 011103 (2014).
- ⁴¹X. Li, S. G. Lu, X. Z. Chen, H. Gu, X. S. Qian, and Q. M. Zhang, *J. Mater. Chem. C* **1**, 23 (2013).