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

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Recommended Citation
Luo, Nengneng; Zhang, Shujun; Li, Qiang; Yan, Qingfeng; He, Wenhui; Zhang, Yiling; and Shrout, Thomas R., "PMN-PT based quaternary piezoceramics with enhanced piezoelectricity and temperature stability" (2014). Australian Institute for Innovative Materials - Papers. 1877.
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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

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

This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/1877
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View online: http://dx.doi.org/10.1063/1.4875797
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Structure, piezoelectric, and ferroelectric properties of BaZrO3 substituted Bi(Mg1/2Ti1/2)O3-PbTiO3 perovskite

Piezoelectric properties and temperature stability of Mn-doped Pb(Mg1/3Nb2/3)-PbZrO3-PbTiO3 textured ceramics

High temperature properties of BiScO 3 – PbTiO 3 piezoelectric ceramics
PMN-PT based quaternary piezoceramics with enhanced piezoelectricity and temperature stability

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(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)PMN-0.10PFN-0.10PZ-xPT 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 \(d_{33} = 640 \text{pC/N}\) 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 \(d_{33}\), 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, Pb(Mg1/3Nb2/3)O3-PbTiO3 (PMN-PT) was reported to possess excellent temperature stability with high Curie temperature \(T_c \approx 130–170^\circ\text{C}\) and much lower rhombohedral to tetragonal ferroelectric phase transition temperature \(T_{c_\text{r}} \approx 50–85^\circ\text{C}\) 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 \(T_{c_\text{r}}/T_c\) to higher temperature by composition tuning, and taking advantage of the engineered domain configuration in single crystals. In the first method, through elements substituting and/or adding of other end-members, new higher \(T_{c_\text{r}}/T_c\) binary and ternary material systems were developed, including Pb(In1/2Nb1/2)-PbTiO3 (PIN-PT),\(^6,7\) Pb(Yb1/2Nb1/2)-PbTiO3 (PYN-PT),\(^8,9\) PbSc1/2(Nb1/2)-PbTiO3 (PSN-PT),\(^10\) Pb(In1/2Nb1/2)-Pb(Mg1/3Nb2/3)O3-PbTiO3 (PIN-PMN-PT),\(^11–15\) Pb(Mg1/3Nb2/3)O3-PbZrO2-PbTiO3 (PMN-PZ-PT),\(^16–19\) and PbSc1/2(Nb1/2)-Pb(Mg1/3Nb2/3)O3-PbTiO3 (PSN-PMN-PT),\(^20\) etc. However, it was found that the temperature stability remained unsolved despite of the high \(T_{c_\text{r}}/T_c\). 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 Bi(Me)O3-PbTiO3 compositions with higher \(T_c > 300^\circ\text{C}\) will shed light on the potentiality of achieving high temperature stability.\(^21–26\) However, except BiScO3-PbTiO3 (BS-PT),\(^21\) the piezoelectric coefficients of the reported Bi(Me)O3-PbTiO3 based ceramics, such as BiFeO3-PbTiO3 (BF-PT),\(^22\) BiInO3-PbTiO3 (BI-PT),\(^23\) Bi(Ni1/2Ti1/2)O3-PbTiO3 (BNT-PT),\(^24\) Bi(Mg1/2Ti1/2)O3-PbTiO3 (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 \(T_c/T_{c_\text{r}}\), 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 \(d_{33}\) in [011]-poled orthorhombic relaxor-PbTiO3 crystals was reported to possess excellent temperature stability with high value being on the order of \(\sim 2100\) 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 \(T_{c_\text{r}}\) with comparable...
piezoelectric properties. The PMN-PZ-PT ternary system, which can be regarded as the combination of PMN-PZ 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. \( \text{Pb} (\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3\) (PFN) is a typical relaxor ferroelectric material with high dielectric permittivity. Through the hybridization of PMN-PT, PZT, and PFN, a quaternary system \((0.85-x)\text{Pb} (\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.10\text{Pb} (\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3-0.05\text{PbZrO}_3-x\text{PbTiO}_3\) (PMN-PFN-PZ-PT) was reported with high \(d_{33}\) > 600 pC/N and enhanced ferroelectric phase transition temperature.

In this work, by tuning the amount of PZ end-member, a quaternary system \((0.80-x)\text{Pb} (\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.10\text{Pb} (\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3-0.10\text{PbZrO}_3-x\text{PbTiO}_3\) 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.

\(0.80-x\)PMN-0.10PFN-0.10PZ-xPT ceramics with \(x = 0.30-0.34\) were prepared by conventional solid state reaction, following the procedure reported earlier. Disk and bar samples with electrodes on the large faces were prepared for the electric properties measurement, as described in the IEEF Standards. The crystal structure of the assintered samples was determined using an X-ray diffractometer (D8 ADVANCE, Brüker, Germany) with Cu K\(_\alpha\) radiation at 20 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 (\(S_{\text{un}}-E\)) 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.

\[
(k_{33})^2 \approx (k_p)^2 + (k_t)^2 - (k_p)^2 (k_t)^2.
\]

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 20 = 44°–46°, which are fitted using the Lorentzian function. The (200)-reflection changes obviously with increasing PT content. When \(x = 0.30\), only a single (200)\(_{\text{R}}\)-peak is observed, indicating a rhombohedral (R) phase; at \(x = 0.34\), the (200)-peak splits into two peaks (200)\(_{\text{T}}\) and (002)\(_{\text{T}}\), 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)\(_{\text{T}}\), (200)\(_{\text{R}}\), and (200)\(_{\text{T}}\), 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 \(\varepsilon_t\) 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 \(\varepsilon_t\) of 2630 and high \(d_{33}\) of 580 pC/N. Fig. 2(b4) gives the field-induced piezoelectric strain coefficient \(d_{33}^*=S_{\text{max}}/E_{\text{max}}\) (\(S_{\text{max}}\) is the maximum strain and \(E_{\text{max}}\) is the maximum electric field, \(\sim 10\) 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(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 $\varepsilon_r$ 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 increased tetragonal component.

The temperature dependence of dielectric permittivity $\varepsilon_r$ and tan $\delta$ of poled samples. (c) Unipolar $S_{uni}-E$ curves at room temperature. (d) Temperature dependence of dielectric permittivity $\varepsilon_r$ and tan $\delta$ of poled samples. (e) Temperature-composition phase diagram of PMN-PFN-PZ-PT quaternary system.
that the variation of $d_{33}^\ast$ 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 ($\geq 20\%$)\textsuperscript{35} and PZT4 ($\sim 15\%$)\textsuperscript{36} ceramics, and outperforms slightly compared with BMT-PT\textsuperscript{25} and BST-PT\textsuperscript{26} which possess much higher Curie temperature of slightly compared with BMT-PT\textsuperscript{25} and BST-PT\textsuperscript{26} which possess much higher Curie temperature of $> 300 \degree C$. In addition, (Na$_{0.49}$K$_{0.49}$Li$_{0.02}$)(Nb$_{0.8}$Ta$_{0.2}$)O$_3$-0.05CaZrO$_3$ (NKL-NT-CZ)\textsuperscript{37} lead-free ceramics exhibit a comparable $d_{33}^\ast$ variation of $\sim 10\%$ in the studied temperature range, however, the value of $d_{33}^\ast$ is 320 pm/V, being only half of that of $x = 0.33$; while Ba(Ti$_{0.8}$Zr$_{0.2}$)O$_3$-50(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ (BZT-50BCT)\textsuperscript{38} has much lower Curie temperature and its $d_{33}$ decreases to nearly 60% of the room temperature value when temperature increases to 70$\degree C$. 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 $d_{33}^\ast$, 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 $\varepsilon_r$, and polarization $P$ contribute to $d_{33}^\ast$, following the equation:\textsuperscript{39}

$$d_{33}^\ast \propto Q\varepsilon_0\varepsilon_rP,$$  

where $\varepsilon_0$ 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.\textsuperscript{40} The equation above suggests that the variation of $d_{33}^\ast$ is mainly related to $\varepsilon_r \times P$. The temperature-dependent maximum polarization $P_{\max}$, remnant polarization $P_r$, coercive field $E_c$, and dielectric permittivity $\varepsilon_r$ 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,\textsuperscript{41} and $E_c$ exhibits the same trend, due to the easier domain wall motion at elevated temperature. On the contrary, $\varepsilon_r$ increases with increasing temperature for both compositions. An abrupt enhancement of $\varepsilon_r$ near the ferroelectric phase transition temperature can be found for $x = 0.30$; while $\varepsilon_r$ is much flatter for $x = 0.33$, due to the smeared free energy barrier between rhombohedral and tetragonal phases. The value of $\varepsilon_r \times P$ for $x = 0.30$ is found to increase with increasing temperature, with inversion point occurring around 115$\degree C$, due to the ferroelectric phase transition, which is consistent with the evolution of $d_{33}^\ast$, as depicted in Fig. 4(a). Of particular importance is that the value of $\varepsilon_r \times P$ for $x = 0.33$ is nearly temperature-independent from 25$\degree C$ to 165$\degree C$, as shown in Fig. 4(b), accounting for the high temperature stability of $d_{33}^\ast$. From the phenomenological descriptions above, it can be concluded that the origin of temperature-insensitive field-induced $d_{33}^\ast$ 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 $\varepsilon_r \times P$, a temperature-insensitive $d_{33}^\ast$ can be expected, this is the case

FIG. 3. (a) Temperature-dependent unipolar strain for $x = 0.33$. (b) Temperature dependence of $d_{33}^\ast$ for ceramics with different PT contents. (c) Comparison of temperature dependence of piezoelectric coefficients for various piezocermics as normalized to their room temperature values $d_{33}^\ast$ for PT-50. The data for PZT5H,\textsuperscript{35} PZT4,\textsuperscript{36} BMN-PT,\textsuperscript{25} BS-PT,\textsuperscript{26} NKL-NT-CZ,\textsuperscript{37} and BZT-50BCT\textsuperscript{38} 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 $k_p$, $k_t$, $k_{33}$, and $d_{31}$ normalized to their room temperature values for $x = 0.33$. 

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high field-induced piezoelectric strain coefficient $d_{33}$ is of 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 $25\text{--}165\degree C$ which is further confirmed by $d_{33}$, making it promising for actuator applications demanding good temperature stability. It is supposed that by shifting or smearing the position tuning, a temperature-insensitive $d_{33}$ can be expected, according to Eq. (1).

In summary, PMN-PFN-PZ-PT ceramics with compositions near MPB were prepared, which exhibit high piezoelectric coefficient near MPB, with $d_{33} = 640 \text{ pC/N}$ and 580 $\text{pC/N}$ 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 $25\text{--}165\degree C$ which is further confirmed by $d_{33}$, 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.