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Piezoelectric properties and temperature stability of Mn-doped $Pb(Mg_{1/3}Nb_{2/3})$-$PbZrO_3$-$PbTiO_3$ textured ceramics

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In this letter, we report the electromechanical properties of textured $0.4Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.25PbZrO_3$–$0.35PbTiO_3$ (PMN-PZT) composition which has relatively high rhombohedral to tetragonal (R-T) transition temperature ($T_{R\text{-}T}$ of 160 °C) and Curie temperature (T_C of 234 °C) and explore the effect of Mn-doping on this composition. It was found that MnO_2-doped textured PMN-PZT ceramics with 5 vol. % $BaTiO_3$ template (T-5BT) exhibited inferior temperature stability. The coupling factor (k_{31}) of T-5BT ceramic started to degrade from 75 °C while the random counterpart showed a very stable tendency up to 180 °C. This degradation was associated with the "interface region" formed in the vicinity of BT template. MnO_2 doped PMN-PZT ceramics textured with 3 vol. % BT and subsequently poled at 140 °C (T-3BT140) exhibited very stable and high k_{31} (>0.53) in a wide temperature range from room temperature to 130 °C through reduction in the interface region volume. Further, the T-3BT140 ceramic exhibited excellent hard and soft combinatory piezoelectric properties of $d_{33} = 720$ pC/N, $k_{31} = 0.53$, $Q_m = 403$, tan $\delta = 0.3\%$ which are very promising for high power and magnetoelectric applications. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3698157]

One of the important issues in high power piezoelectric devices is heat generation under large AC resonant drives that significantly affects the device performance.[1] In order to withstand the degradation under high power conditions, the piezoelectric material should possess high mechanical quality factor (Q_m) and low dielectric loss (tan δ) along with high phase transition temperatures. In addition, high electromechanical coupling coefficient (k) of piezoelectrics is necessary for effective electric to mechanical energy conversion, and high strain coefficient (d) is important for high vibration velocity ($v_{rms} \propto Q_m \cdot d$). Therefore, designing high power piezoelectric materials involves consideration of "hard" and "soft" combinatory characteristics. These combinatory characteristics are also of importance in designing magnetoelectric (ME) laminate composites operating in the vicinity of electromechanical resonance.[2,3] Realization of piezoelectric material with "hard" and "soft" combinatory properties is quite challenging since the "hard" characteristics (high Q_m and low tan δ) are originated from "pinned" ferroelectric domain state which usually degrades the "soft" characteristics (high d and high k) of piezoelectrics.[4]

Texturing (grain orientation along specific crystallographic direction) is suitable for engineering ferroelectric domain state of piezoelectric ceramics.[5–9] By using templated grain growth (TGG) method, highly ⟨001⟩ textured piezoelectric ceramics with high d and high k, which are comparable with those of ⟨001⟩ single crystal piezoelectrics (e.g., rhombohedral $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN-PT)), have been developed.[9] Since TGG method is based on tape casting and conventional sintering process, the textured piezoelectric ceramics can be cost-effectively synthesized in requisite dimensions as compared to expensive single crystal piezoelectrics. Mn-ion is well-known as a dopant for inducing "hard" characteristics and enhancing the Q_m of Pb-based perovskite (ABO_3) piezoelectric materials. Several studies have reported that incorporation of Mn-ion onto the B-site of perovskite creates oxygen vacancies resulting in pinned domain wall motion.[4,10,11] Based on these prior investigations, one good concept for designing high power combinatory piezoelectrics is integration of texturing (to enhance "soft" characteristics) and Mn-doping (to enhance "hard" characteristics). However, the temperature instability of piezoelectric properties in textured ceramics synthesized by TGG method using heterogeneous template could be problematic. To exemplify, in the case of the textured PMN-PT with $SrTiO_3$ (ST) templates the maximum dielectric constant (K_{max}) and (T_{max}) decreases with the addition of ST (T_{max} was found to be 158, 147, and 120 °C for 1, 3, and 5 vol. % ST samples, respectively).[9] Further, in this case the depolarization temperature was found to be quite low on the order of 60 °C.[9] The main reason behind this degradation was the dissolution of Sr^{2+} in PMN-PT due to poor chemical stability of ST in PbO environment. For $0.4(Na_{1/2}Bi_{1/2})TiO_3$-$0.6PbTiO_3$ (NBT-0.6PT) textured PMN-PT, the d_{33} was found to deteriorate at 60 °C due to decrease of $T_{R\text{-}T}$ and T_{max}.[12] In order to avoid these problems, we selected $0.4Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.25PbZrO_3$–$0.35PbTiO_3$ (PMN-PZT) composition as the baseline since it has relatively high rhombohedral to tetragonal (R-T) transition temperature ($T_{R\text{-}T}$ of 160 °C) and Curie temperature (T_C of 234 °C) compared to that of PMN-PT. This composition was then modified by Mn-doping and textured using $BaTiO_3$ templates to achieve superior performance with temperature stability.

1 mol. % MnO_2 doped PMN-PZT ceramic was textured by TGG method with $BaTiO_3$ (BT) template crystals using tape casting and sintering process described in detail elsewhere.[7] For comparison, randomly oriented pure PMN-PZT

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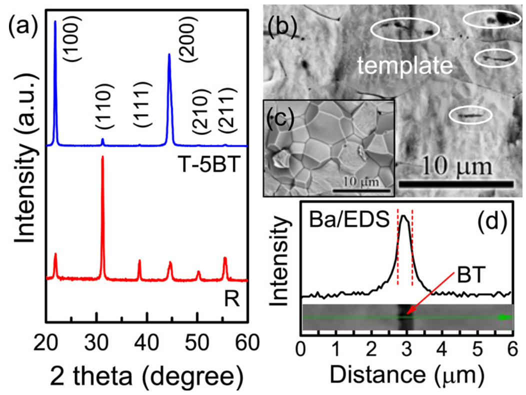

FIG. 1. (a) XRD patterns of randomly oriented and textured MnO_2 doped PMN-PZT ceramics with 5 vol. % BT template (abbreviated as R and T-5BT, respectively); SEM images of (b) T-5BT and (c) R ceramic; (d) line scanning element analysis of EDS across BT and PMN-PZT matrix.

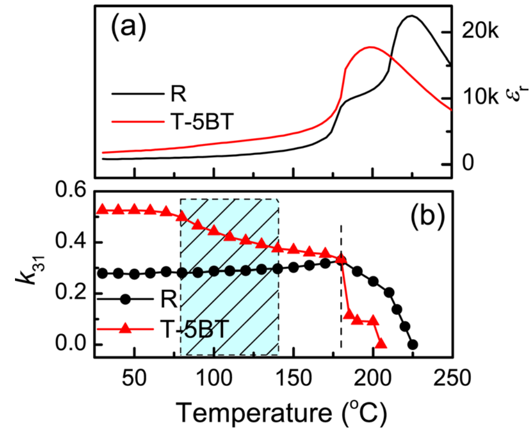

FIG. 2. (a) Dielectric constant ($\varepsilon_{33}{}^T/\varepsilon_0$) and (b) electromechanical coupling coefficient (k_{31}) of R and T-5BT ceramic as a function of temperature.

and 1 mol. % MnO_2 doped PMN-PZT were also synthesized by using the same process without employing BT template. The structural properties of samples were determined using x-ray diffraction (XRD, PANalytical X'Pert, CuKα, Philips, Netherlands) and scanning electron microscopy (SEM, FEI Quanta 600 FEG, Philips). The degree of pseudo-cubic ⟨001⟩ texturing of samples was determined by Lotgering factor method.[13] The dielectric constant ($\varepsilon_{33}{}^T/\varepsilon_0$) and tan δ of poled samples was measured as a function of temperature by using a multi-frequency LCR meter (HP4274A, Hewlett-Packard Development Company, CA). Pyroelectric current was measured as a function of temperature by using a pA meter (HP 4140B, USA). The piezoelectric properties of samples were obtained by resonance and anti-resonance technique using impedance/gain phase analyzer (HP 4194A, Hewlett-Packard Development Company) and d33-meter (YE 2730 A, APC Products, Inc., PA).

Figure 1(a) shows the XRD patterns of randomly oriented and textured MnO_2-doped PMN-PZT ceramics with 5 vol. % BT (R and T-5BT ceramics, respectively). All the samples showed perovskite structure. Compared to the R ceramic, the *00l* reflection peaks of T-5BT ceramic were enhanced exhibiting high Lotgering factor of 96% that indicates a strong pseudo-cubic ⟨001⟩ orientation of textured grains in the T-5BT ceramic. The SEM image of the T-5BT ceramic showed a brick wall-like microstructure with well aligned BT templates (black lines) in the matrix as shown in Fig. 1(b) while the R ceramics showed homogeneous equiaxed grains (Fig. 1(c)). Table I shows the dielectric and piezoelectric properties of randomly oriented pure PMN-PZT (R-pure ceramic), R ceramic, and T-5BT ceramic poled and measured at room temperature. The piezoelectric properties of T-5BT ceramic were enhanced compared to those of R-pure and R ceramics. Note that the Q_m and tan δ of the T-5BT ceramic were improved together with the *d* and *k* coefficients clearly demonstrating presence of "hard" and "soft" combinatory characteristics. Both d_{33} and Q_m of the T-5BT ceramic were 4 times higher and tan δ was 6.5 times lower than those of R-pure ceramic. This result confirms that the combination of texturing and Mn-doping is effective for developing high power piezoelectrics.

Figure 2(a) shows the dielectric permittivity as a function of temperature for random and textured Mn doped PMN-PZT ceramics. There are two obvious peaks for random ceramics located at ∼180 °C and 225 °C. The first dielectric anomaly is the rhombohedral to tetragonal phase transformation temperature (T_{R-T}), while the second one is related to the Curie temperature (T_C). For textured ceramics, there is only one obvious peak located at 198 °C attributed to T_C. The decrease of T_C is due to the existence of low T_C BT template indicating shift in the composition towards rhombohedral side. Several other studies have reported that T_C of textured PMN-PT ceramics is decreased due to the existence of heterogeneous templates (such as $BaTiO_3$, $SrTiO_3$).[9,14] In case of $SrTiO_3$ textured PMN-PT, the depolarization temperature was unacceptably low (∼60 °C).[9] In contrast, the T_C of T-5BT textured ceramics was still high on the order of 198 °C. However, we found that T-5BT ceramic has problem related to temperature stability of piezoelectric properties. As it can be seen in Fig. 2(b) that the k_{31} of T-5BT ceramic started to degrade from 75 °C while the R ceramic showed a stable tendency up to 180 °C ($T_{R\text{-}T}$ of R ceramic). In order to understand this problem, we first analyzed the spontaneous polarization of T-5BT ceramic to precisely confirm the contribution of R-T transition. The pyroelectric current (I_P) of the ferroelectrics under variation of temperature is given as

TABLE I. Dielectric and piezoelectric properties of randomly oriented pure PMN-PZT, randomly oriented, and textured MnO_2 doped PMN-PZT ceramics (abbreviated as R-pure, R, and T-5BT, respectively).

Properties	$\varepsilon_{33}{}^T/\varepsilon_0$	tan δ (%)	d_{33} (pC/N)	D_{31} (pC/N)	k_{31}	g_{33} (10^{-3}Vm/N)	g_{31} (10^{-3}Vm/N)	Q_m	T_m (°C)
R-pure	915	1.9	230	−78	0.27	28	−9.6	102	234
R	765	0.32	180	−69	0.27	27	−10	747	225
T-5BT	1723	0.29	680	−230	0.52	45	−15	428	198

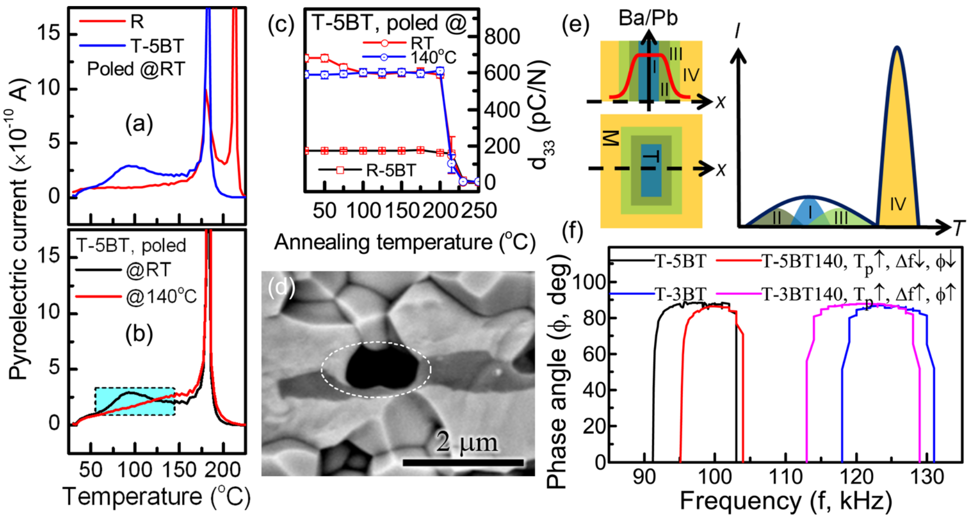

FIG. 3. Pyroelectric current vs. temperature curves of (a) R and T-5BT ceramics poled at room temperature and (b) T-5BT ceramics poled at room temperature and 140 °C; (c) d_{33} of R and T-5BT ceramics poled at room temperature and 140 °C as a function of annealing temperature; (d) SEM of partially dissolved BT template; (e) schematic diagram of the concentration gradient that exists in the vicinity of the template–matrix interface; (f) the effect of the poling temperature and template content on degree of poling condition.

$I_P = (dP_s/dT)\cdot(dT/dt)$, where P_s is spontaneous polarization, T is temperature, and t is time. Usually, the I_P of ferroelectrics shows a sharp increase at phase transition temperatures (e.g., at $T_{R\text{-}T}$ and T_C of R ceramic as shown in Fig. 3(a)). The T-5BT ceramic also exhibited a sharp I_P peak at 180 °C; however, there was another broad peak in the range 75–140 °C. There was no obvious $T_{R\text{-}T}$ peak of T-5BT ceramic in Fig. 2(a); therefore, this peak was not associated with the rhombohedral-tetragonal phase transition. Figure 3(b) shows the I_P vs. temperature curve of the T-5BT ceramic poled at 140 °C. It can be clearly seen in this figure that broad peak found in Fig. 3(a) in the region 75–140 °C has vanished. Since the T_C of BT is 120 °C, the BT template in T-5BT ceramic could be depoled at higher temperature. However, starting temperature of degradation was much lower than 120 °C as seen in Fig. 2(b) and more obvious in the d_{33} plot shown in Fig. 3(c). This result indicates that the depoling of BT templates is not the sole reason for electromechanical degradation and broad peak in the Fig. 3(a) and gave us insight to consider the role of template and template-matrix interface.

Although BT is quite stable in textured PMN-PT ceramic,[15] it is known to dissolve in PZT ceramics.[16] In the case of PMN-PZT, we investigated the microstructure of T-5BT ceramic in detail and found that some of the porous BT templates were partially dissolved during the texturing process (Fig. 3(d)). Figure 3(e) schematically illustrates the concentration gradient that exists in the vicinity of the template–matrix interface using the microstructure and EDS analysis. There are four distinct regions in this diagram. Region I corresponds to the pure BT template, region II corresponds to the diffused area with high Ba/Pb concentration, region III corresponds to the region with slightly lower concentration ratio of Ba/Pb, and region IV represents pure matrix composition or no Ba. The diffusion of Ba into the matrix was confirmed from EDS line scanning data (Fig. 1(d)) showing that "interface region" with the width of ~1 μm was formed in the vicinity of BT template. The interface region could have composition corresponding to mixture of perovskites (Pb, Ba)[($Mg_{1/3}Nb_{2/3}$),Zr,Ti)]O_3 and the T_C of the interface region can be lowered depending upon the concentration of Ba. All the component systems corresponding to PMN, BMN, BZ have been shown to have much lower T_C than BT.[17–19] Thus, the variation of Ba/Pb concentration across this interface region results in the wide depoling temperature range which explains the broad pyroelectric current peak in Fig. 2(a) as schematically depicted in Fig. 3(e). Therefore, the degradation between 75 to 140 °C can be associated with the depoling of template which has lower paraelectric-ferroelectric transition temperature and the formation of interface region.

In this scenario, the piezoelectric properties of the system can be controlled by: (i) lowering the template content and (iii) poling the ceramic at temperatures higher than T_C of template and interface region. Based on this hypothesis, the content of BT template was decreased to reduce the interface volume in the ceramic and poling temperature was increased

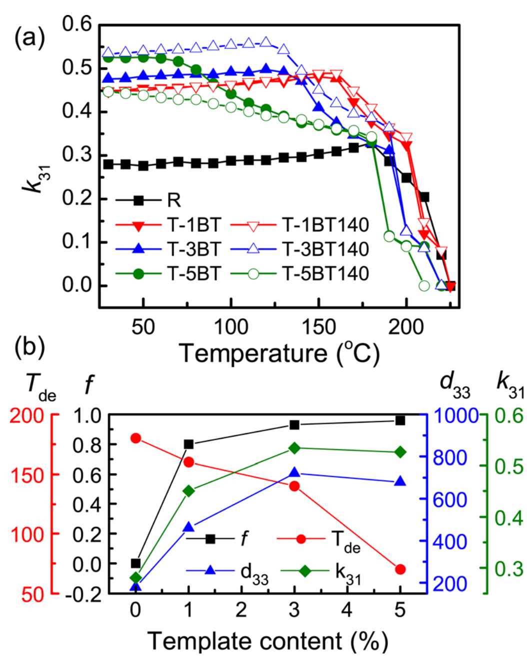

FIG. 4. (a) k_{31} vs. temperature characteristics of randomly oriented and textured MnO_2 doped PMN-PZT ceramics with 1, 3, and 5 vol. % BT template poled at 140 °C (abbreviated as R, T-1BT140, T-3BT140, and T-5BT140, respectively); (b) Lotgering factor (f), degradation temperature (T_{de}), d_{33} and k_{31} of textured MnO_2 doped PMN-PZT ceramics as a function of BT template content.

TABLE II. Dielectric and piezoelectric properties of representative textured perovskite ceramics.

Composition	Template	F (%)	T_C (°C)	T_{de} (°C)	d_{33} (pC/N)	k_{31}	Q_m	tan δ (%)
BNT-BT[a]	$Bi_4Ti_3O_{12}$	96	260	–	241	–	–	–
KNNS[b]	$NaNbO_3$	98	353	160	208	0.37	–	1.8
KNN (LF4)[c]	$NaNbO_3$	91	253	–	416	–	–	–
$Ba(Zr_{0.085}Ti_{0.915})O_3$[d]	5 vol. % $SrTiO_3$	>90	95	–	975[j]	–	–	–
PMN-32.5PT[e]	5 vol. % $BaTiO_3$	90	165	–	1150[j]	0.484	–	1.3
PMN-32PT[f]	5 vol. % $BaTiO_3$	97	147	–	877[j]	–	–	–
PMN-32.5PT[g]	5 vol. % $SrTiO_3$	69	120	60	1660[j]	–	–	2
PMN-34.5PT[h]	PMN-PT	95	161	–	660	0.44	110	–
PMN-25PT[i]	7 vol. % NBT-0.6PT	92	129	60	852[j]	0.54	94	1.0
2% Mn+PMN-25PT[i]	7 vol. % NBT-0.6PT	49	130	75	517[j]	0.44	714	0.5
1% Mn+PMN-PZT	3 vol. % $BaTiO_3$	93	210	130	720	0.53	403	0.3

[a]Reference 8.
[b]Reference 20.
[c]Reference 6.
[d]Reference 21.
[e]Reference 15.
[f]Reference 14.
[g]Reference 9.
[h]Reference 22.
[i]Reference 12.
[j]d_{33} was computed from strain-electric field curves at low field.

to 140 °C. Figure 3(f) shows the effect of the poling temperature and template content. A much higher degree of poling was found in the T-3BT ceramic poled at 140 °C confirming our hypothesis.

Figure 4(a) shows the k_{31} vs. temperature curves of MnO_2 doped PMN-PZT ceramics textured with 1, 3, and 5 vol. % BT and subsequently poled at 140 °C (T-1BT140, T-3BT140 and T-5BT140 ceramics, respectively). The T-5BT140 ceramic showed a gradual declining tendency in k_{31} even though the degradation slope was decreased as compared to that of T-5BT ceramic, illustrating the significance of Ba diffusion and formation of the interface region. However, the 3BT140 ceramic exhibited quite stable and high k_{31} (>0.53) in a wide temperature range from room temperature to 130 °C. This result confirms that as the volume of interface region which has low T_C and relatively poor piezoelectricity was decreased by decreasing the BT content, an improved k_{31} with high degradation temperature (T_{de}) was obtained. Furthermore, there was no obvious change in k_{31} around 120 °C indicating that the formation of interface region is dominant factor in the degradation rather than the depoling of pure BT template. In the case of T-1BT140 ceramic, the T_{de} was increased up to 160 °C due to further reduced volume of interface region; however, the k_{31} value was decreased because of low texture degree (Lotgering factor of 80%) as shown in Fig. 4(b).

Table II lists the dielectric and piezoelectric properties of representative textured perovskite piezoelectric ceramics. Prior research has mostly focused on texturing "soft" piezoelectric compositions in order to improve d_{33}. Recently, results on Mn-doped PMN-PT textured ceramics were reported demonstrating good piezoelectric properties along with improved Q_m ($d_{33} = 517$ pC/N, $k_{31} = 0.44$, $Q_m = 714$, tan $\delta = 0.5\%$, and $T_{de} = 75$ °C).[12] In comparison, the 3BT140 ceramic synthesized in this study exhibited excellent "hard" and "soft" combinatory piezoelectric properties of $d_{33} = 720$ pC/N, $k_{31} = 0.53$, $Q_m = 403$, tan $\delta = 0.3\%$, along with good temperature stability ($T_{de} = 130$ °C).

In summary, we investigated the piezoelectric properties of textured MnO_2 doped PMN-PZT ceramics. The combination of texturing and hardening effect was confirmed to be suitable for developing high power piezoelectric materials possessing excellent "hard and soft" combinatory characteristics. The effect of template content on temperature stability of piezoelectric properties was investigated. The results show that the content and chemical stability of BT template significantly affects the piezoelectric properties and temperature stability of PZT-based textured ceramics. Mn-doped PMN-PZT textured ceramics containing 3 vol% BT exhibited excellent piezoelectric properties $d_{33} = 720$ pC/N, $k_{31} = 0.53$, $Q_m = 403$, tan $\delta = 0.3\%$ along with good temperature stability ($T_{de} = 130$ °C).

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