J Electroceram (2010) 24:294–299
DOI 10.1007/s10832-009-9571-1

Temperature- and dc bias field- dependent piezoelectric effect of soft and hard lead zirconate titanate ceramics

Fei Li · Zhuo Xu · XiaoYong Wei · Xi Yao

Received: 1 July 2008 / Accepted: 30 March 2009 / Published online: 9 April 2009

Abstract The dc bias field-dependent piezoelectric coefficient d_{33} of lead zirconate titanate ceramics (PZT5, PZT8 and P5H) were determined by a quasi-static method. It was found that piezoelectric coefficient d_{33} was almost independent of positive dc bias field for PZT8 and PZT5 ceramics, while for P5H ceramic an obvious decrease of coefficient d_{33} was observed under positive dc bias field. On the other hand, the temperature-dependent piezoelectric response for PZT ceramics were investigated by both quasi-static and resonance methods. The piezoelectric coefficient d_{33} was found to increase with increasing temperature for both PZT5 and PZT8 ceramics. For P5H ceramics, coefficient d_{33} showed a first decreasing and then increasing tendency with respect to temperature. These results were discussed in terms of intrinsic and extrinsic contributions to piezoelectric response.

Keywords Temperature · dc bias field · Piezoelectric effect · PZT ceramics

1 Introduction

Because of the high piezoelectric properties close to the morphotropic phase boundary (MPB), the ceramic solid solution $PbZr_{1-x}Ti_xO_3$ (known as PZT) has been widely used as piezoelectric materials in sonars, hydrophones, ultrasound generators, high-voltage generators, micro-positioners, etc [1]. In order to achieve large actuation, high electric field is usually applied to the piezoelectric materials. In addition, the piezoelectric materials would be used on a wide temperature range for some special applications (e.g., underwater device and transducer for well logging). Therefore, it is very important to study the temperature- and dc bias field-dependent piezoelectric response of PZT piezoelectric ceramics. Although a number of studies have been focused on the temperature- and dc bias field-dependent piezoelectric response through converse piezoelectric response [2–4], evaluation of these dependences through direct piezoelectric effect is still expected.

The purpose of the present paper is to determine the temperature- and dc bias field-dependent piezoelectric coefficient d_{33} through direct piezoelectric response of PZT ceramics. Moreover, the temperature dependence of dielectric permittivity ε_{33}, piezoelectric coefficient d_{33} and electromechanical coupling factor k_{33} are also evaluated by resonance method.

2 Experimental method

2.1 Quasi-static method

The direct piezoelectric coefficient d_{33} can be derived from Eq. 1:

$$D_3 = d_{33}\sigma_3 \tag{1}$$

where D_3 is electric displacement, σ_3 is uniaxial stress. To investigate the relationship between direct piezoelectric response and dc bias field, the experimental setup is designed and shown in Fig. 1. The alternative stress is applied by a ZJ-27 d_{33}-meter (Institute of Acoustics, Chinese Academy of Sciences). The dc bias field is applied

F. Li (✉) · Z. Xu · X. Wei · X. Yao
Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China
e-mail: lifei1216@gmail.com

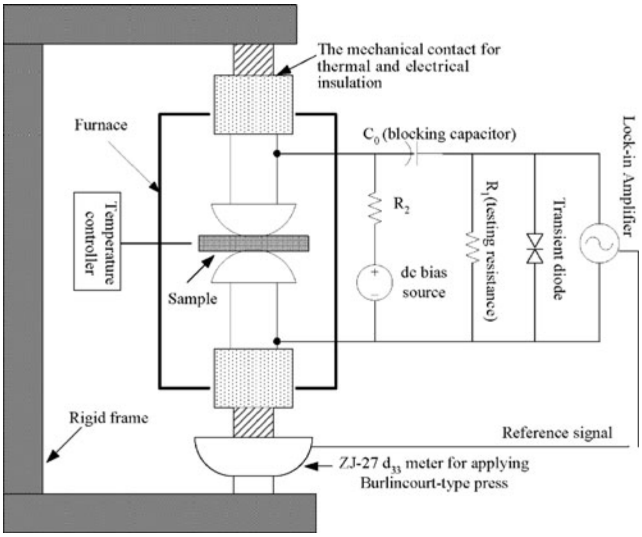

Fig. 1 Experimental setup for measuring the dc bias field-dependent of piezoelectric coefficient d_{33} by the quasi-static method

by a high voltage source (SRS 350, Stanford Research Systems). Here capacitor C_0 is employed to block the dc signal. The generated piezoelectric charge is measured via a "shunt" resistance R_1. The capacitance of the sample (C_s), blocking capacitance C_0, and resistance R_1 and R_2 satisfied the relationship: $C_0 >> 1/\omega R_1 >> C_s >> 1/\omega R_2$. By analyzing the experimental circuit, the voltage through R_1 can be expressed as:

$$V_1 = I_1 R_1 = \frac{dQ}{dt} R_1 = A \frac{d\sigma_3 e^{j\omega t} d_{33}}{dt} R_1 = j\omega R_1 F_3 d_{33} e^{j\omega t} \tag{2}$$

where ω (about 2π × 110 in our measurement) and F_0 (about 0.5 N) are angle frequency and amplitude of applied alternative force, respectively. d_{33} is piezoelectric coefficient, t is time. In this experimental system, voltage V was measured by a Lock-in amplifier (SRS830, Stanford research system).

2.2 Resonance method

To resonance method, piezoelectric coefficient can be obtained from the sample with a suitable shape and orientation [5]. The resonance, antiresonance frequencies and dielectric permittivity ε^T must be determined to calculate the piezoelectric coefficient. In our experiments, the long and thin rod samples with large length-to-width ratios (*l/w>>5*) and electroded at both ends are used to measure the longitudinal piezoelectric coefficient d_{33}, according to the following equations:

$$k_{33}^2 = \frac{\pi}{2}\frac{f_a}{f_r}\cot\left(\frac{\pi}{2}\frac{f_a}{f_r}\right) \tag{3}$$

$$s_{33}^D = \frac{1}{4\rho (lf_a)^2} \tag{4}$$

$$s_{33}^E = \frac{s_{33}^D}{1 - k_{33}^2} \tag{5}$$

$$d_{33} = k_{33}\sqrt{s_{33}^E \varepsilon_{33}^T} \tag{6}$$

where l and w are length and width of the sample, respectively.

In addition, it should be noted that the results calculated according to IEEE standard are accurate only if the mechanical loss of piezoelectric vibrator is small [6, 7], which means that the maximum phase angle of vibrator should approach 90º. Admittedly, the piezoelectric coefficients measured by resonance method are based on the converse piezoelectric effect, since the piezoelectric vibration is excited by alternative electric field.

3 Experimental procedure

PZT samples (PZT5, PZT8 and P5H) were obtained from BaoDing HongSheng Acoustics Electron Apparatus Co., Ltd. The composition of these commercial ceramics is around the morphotropic phase boundary (MPB) and the details were presented in Table 1. The long and thin rod samples with dimensions 10 mm (poled)×2 mm×2 mm were used to determine the temperature-dependent piezoelectric response. The specimens with dimensions 0.5 mm× 3 mm× 3 mm and electroded on the main surfaces were adopted to determine the dc bias field-dependent piezoelectric coefficient d_{33}.

To determine the temperature-dependent piezoelectric coefficient d_{33} and electromechanical coupling factor k_{33} by

Table 1 Characteristics of PZT5, PZT8 and P5H piezoelectric ceramics at room temperature.

	T_c [ºC]	$\varepsilon_{33}^T/\varepsilon_0$	tgδ [%]	d_{33} [pC/N]	Q_m	k_{33}	dopant	type
PZT5	260	1600	1.8	420	100	0.70	Li^+, Sb^{5+}	soft
PZT8	280	1300	0.29	220	1100	0.52	Fe^{3+}	hard
P5H	170	3600	2.3	650	70	0.68	Mg^{2+}, Nb^{5+}	softest

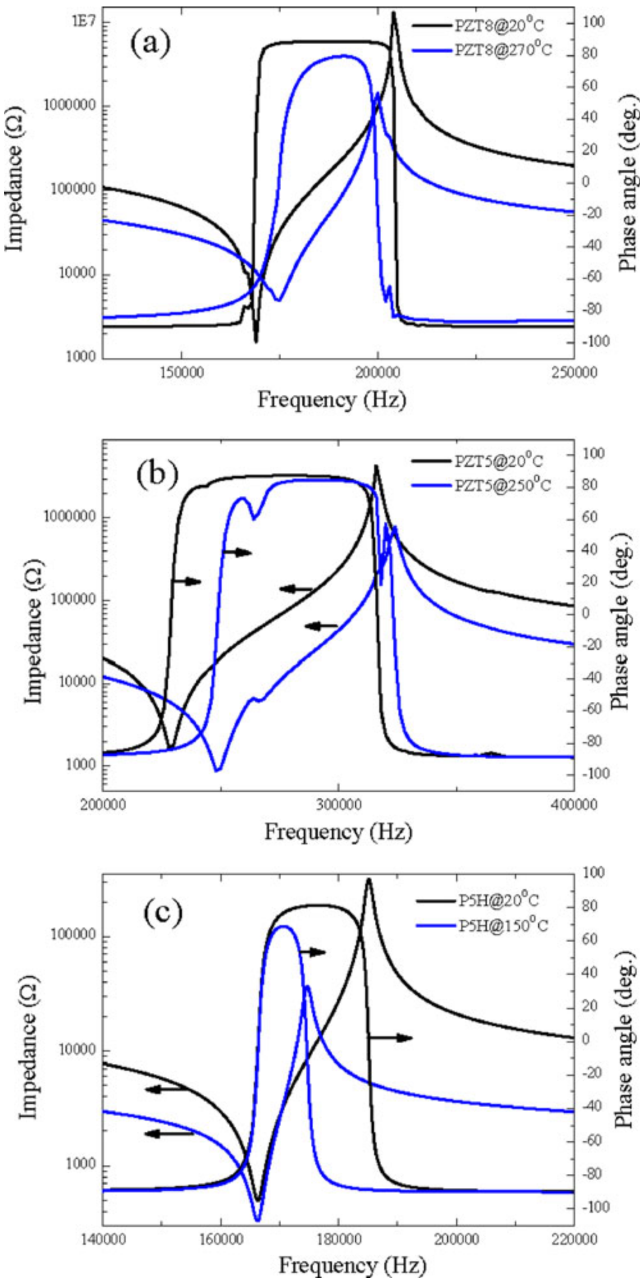

Fig.2 The impedance and phase angle spectrum of 33-mode vibrators for (**a**) PZT5, (**b**) PZT8 and (**c**) P5H

resonance method, an impedance analyzer (HP-4294A, Hewlett-Packard) was used to measure the impedance spectrum of PZT vibrators and the sample holder was settled in a furnace. In addition, the Hewlett-Packard 16048A 1 m probe extension was installed to connect the impedance analyzer and sample holder. In this experiment, the temperature was raised from 20ºC to 300ºC and maintained about 5 min at every testing temperature in order to achieve thermal equilibration in furnace. On the other hand, the equipment depicted in Section 2.1 was used to measure the temperature and dc bias field-dependent d_{33} through direct piezoelectric effect, where the dc bias field was cycled from 3000 V/mm to −3000 V/mm. At each testing point, the dc bias field was maintained about 2 min in order to obtain a stable piezoelectric-induced charge signal.

4 Experimental results and discussion

4.1 Temperature dependence of piezoelectric response for PZT ceramics

Figure 2 shows the impedance and phase angle spectrum of 33-mode PZT vibrators. It is found that the maximum phase angle approaches 90º even at high temperature (for PZT5, maximum phase was 81º at 250ºC; for PZT8, maximum phase was 83º at 270ºC; for P5H, maximum phase was 70º at 150ºC), which means that the effect of mechanical loss could be ignored and the results determined by resonance method are accurate upon the whole temperature range.

Figure 3 shows the temperature-dependent piezoelectric coefficient d_{33} of PZT5, PZT8, and P5H ceramics. It is suggested that the variation tendency of piezoelectric coefficient d_{33} determined by the quasi-static method is similar to that determined by resonance method, although there are some differences between the levels of coefficient d_{33} determined by these two methods. Those differences can be attributed to the differences of the experimental frequencies, equipments and theories (from direct and converse piezoelectric effects) between resonance and quasi-static method. It is also seen from Fig. 2 that piezoelectric coefficient d_{33} increases with temperature for PZT5 (from 420 pC/N to 577 pC/N, increasing about 36%) and PZT8 (from 220 pC/N to 340 pC/N, increasing about

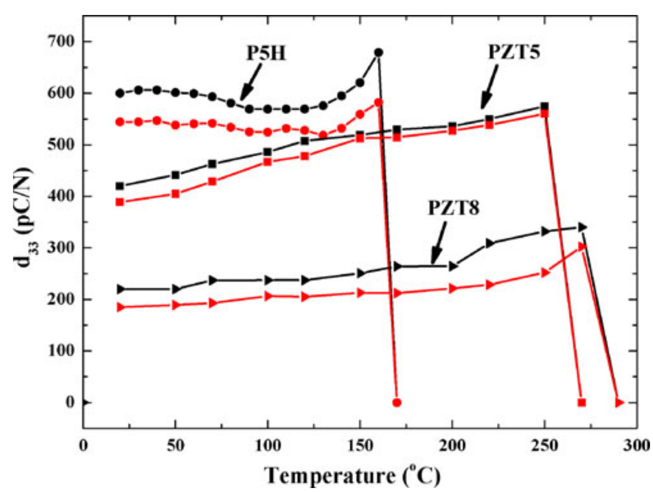

Fig. 3 Temperature-dependent piezoelectric coefficient d_{33} of PZT ceramics. The *red line* was determined by the resonance method; the *black line* was determined by the quasi-static method

55%), while for P5H ceramic d_{33} firstly decreases and then increases with temperature. In other published results, the d coefficients generally increase with increasing temperature for Pb-based ferroelectrics [4, 8–10].

As temperature increases, the enhancement of piezoelectric coefficient d_{33} of PZT5 and PZT8 ceramics is due to the following mechanisms: (1) the intrinsic piezoelectric response of PZT in single domain will increase, as calculated in Ref. [11]; (2) the extrinsic piezoelectric response (contribution of domain switching [12, 13]) will also increase, because the thermal energy of domains will decrease and lower activation energy will be required to make domains change from one minima state to another.

Admittedly, the thermal depoling effect could make the piezoelectric response decrease with increasing temperature. For P5H ceramic, because it is the softest ceramic among those different ceramics, the depoling effect is more obvious, resulting in a decrease of piezoelectric coefficient d_{33} with increasing temperature from 20ºC to 130.

Figures 4 and 5 show the dielectric permittivity and electromechanical coupling factor as a function of temperature respectively. It can be found from Figs. 3 and 4 that the increase of ε_{33} is larger than that of d_{33} with increasing temperature. Thus, in Fig. 5 the decreasing tendency of coupling factor k_{33} ($k_{33} = d_{33} \Big/ \sqrt{s_{33}^E \varepsilon_{33}^T}$) with respect to temperature is observed for PZT5, PZT8 and P5H ceramics. In addition, it also can be seen from Fig. 5 that PZT8 ceramic possesses a more stable coupling factor k_{33} with respect to temperature when compared with PZT5 and P5H.

4.2 dc bias field dependence of piezoelectric response of PZT ceramics

The d_{33}-vs-E curves for PZT8 ceramic at various temperatures are displayed in Fig. 6. Figure 6(a) shows that

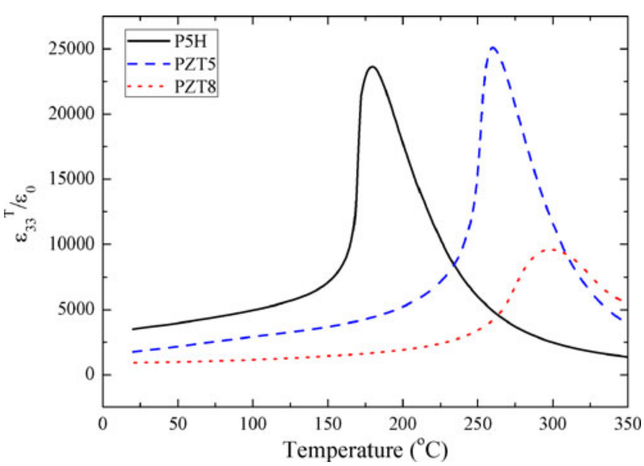

Fig. 4 Dielectric permittivity measured at 1 kHz as a function of temperature

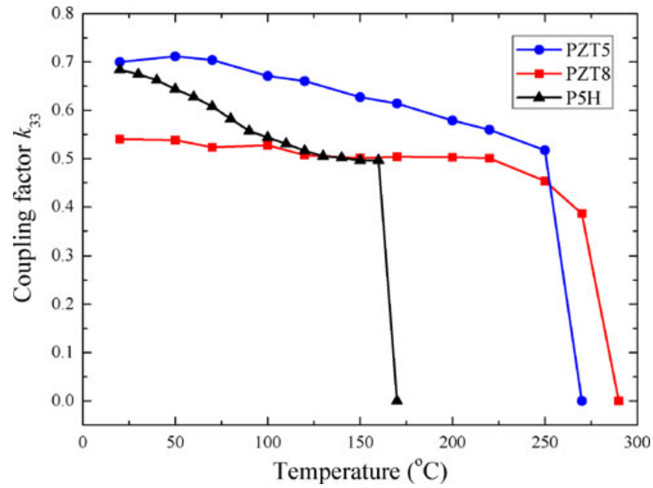

Fig. 5 Temperature dependent electromechanical coupling factor k_{33} of three different PZT ceramics

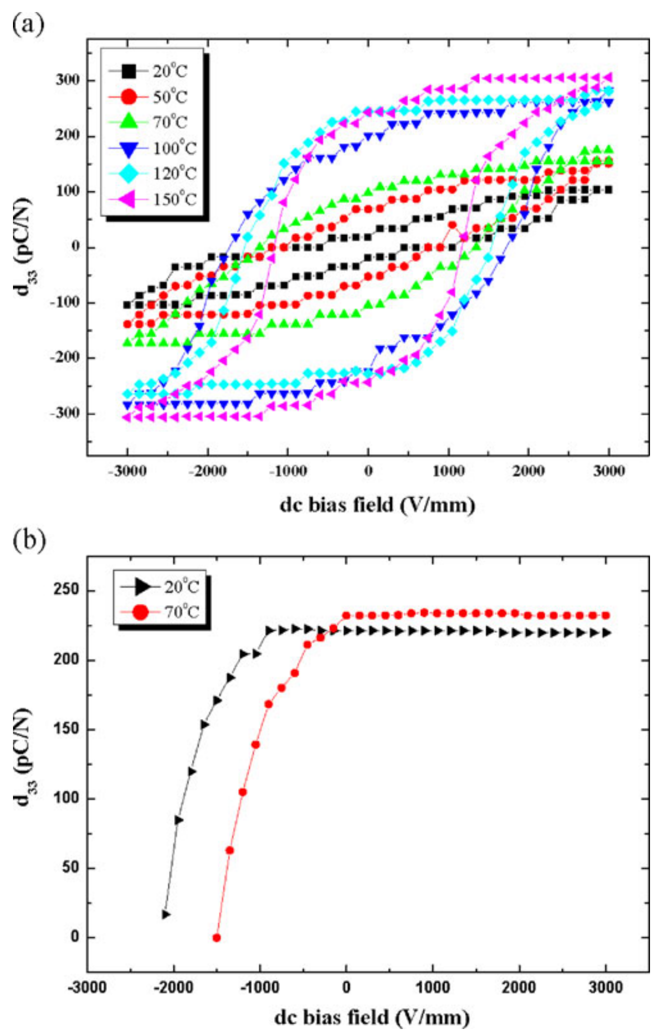

Fig. 6 dc bias field-dependent piezoelectric coefficient d_{33} of PZT8. (**a**) PZT8; (**b**) well-poled PZT8

3000 V/mm is not high enough to pole PZT8 samples at the temperature below 70ºC. Thus we also measured the dc bias field dependence of piezoelectric coefficient d_{33} of well-poled PZT8 below 70ºC, as shown in Fig. 6(b). Figure 7(a) and (b) show the dc bias field-dependent piezoelectric coefficient d_{33} of PZT5 and P5H. It is obvious that the dc bias field-dependent piezoelectric coefficient d_{33} for PZT8 is similar to that of PZT5.

As the dc bias field decreases from 3000 V/mm to 0 V/mm, the piezoelectric coefficient d_{33} of both PZT5 and PZT8 decreases, and this is more obvious at higher temperature. By decreasing the positive dc bias field some domains are reversed in order to minimize the electric free energy, which could lead to a decrease of piezoelectric response. On the other hand, for P5H the coefficient d_{33} firstly increases and then decreases as the positive dc bias field deceases from 3000 V/mm to 0 V/mm. Similar responses in (720) oriented $BaTiO_3$ single crystal [14] are also reported. This enhancement of d_{33} with decreasing positive dc bias field can be attributed to the influence of positive dc bias field on extrinsic piezoelectric response. With decreasing positive dc bias field (from 3000 V/mm), extrinsic piezoelectric response will increase because the clamping effect induced by positive dc bias field will abate.

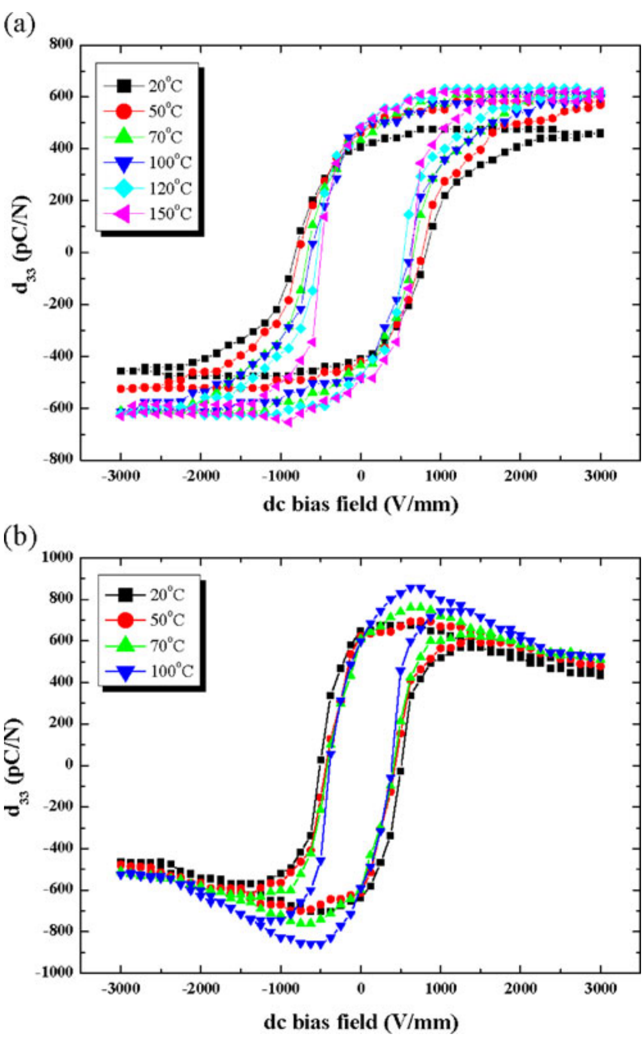

Fig. 7 dc bias field-dependent piezoelectric coefficient d_{33} of (**a**) PZT5 and (**b**) P5H

Under negative dc bias field, the variation tendencies of piezoelectric coefficient d_{33} are similar among those PZT ceramics. Piezoelectric coefficient d_{33} rapidly abates as the negative dc bias field approaches coercive electric field (E_c). At the coercive electric field, domains will be reversed to opposite direction compared with the original direction through a nucleation and growth process (depoling process), which could lead to a lowering of piezoelectric response.

On the other hand, the piezoelectric response of PZT ceramics (EC69 and EC65) is reported to increase with increasing negative dc bias field in Ref. 2, where the increase is attributed to the increase of extrinsic piezoelectric response by depinning and deaging effects. We believe that this extrinsic contribution is relatively small in our experiments because the applied stress signal is rather small (0.02 MPa). As the analysis in Ref. [15], the extrinsic piezoelectric response will be decreased by decreasing amplitude of testing signal. Moreover, this extrinsic contribution might be concealed by the depoling effects with increasing negative dc bias field. Thus, it is reasonable that piezoelectric coefficient d_{33} doesn't show any increase with increasing negative dc bias field in our experiments.

5 Conclusion

Temperature- and dc bias field- dependent piezoelectric coefficient d_{33} have been evaluated through direct piezoelectric effect of PZT5, PZT8 and P5H piezoelectric ceramics. The results showed that PZT5 and PZT8 ceramics are more proper to be used in some high temperature applications, although the piezoelectric response of P5H is larger than that of PZT5 and PZT8 at room temperature. In addition, compared with P5H, the piezoelectric response of PZT8 and PZT5 are more stable under dc bias field. These data could provide a basis for future piezoelectric device design.

Acknowledgment This work was financially supported by the National Basic Research Program of China (973 Program)(Grant No.2009CB623306) and the National Natural Science Foundation of China (Grant No. 60528008) and the Key Science and Technology Research Project from the Ministry of Education of China (Grant No.108180).

References

1. Y.H. Xu, *Ferroelectric materials and their applications* (North-Holland, Amsterdam, 1991)
2. A.J. Masys, W. Ren, G. Yang, B.K. Mukherjee, J Appl Phys **94**, 1155 (2003). doi:10.1063/1.1587008
3. N. Uchida, T Ikeda Jpn J Appl Phys J **4**, 867 (1965). doi:10.1143/JJAP.4.867
4. R. Sabat, B.K. Mukherjee, W. Ren, G Yang. J Appl Phys **101**, 064111 (2007). doi:10.1063/1.2560441
5. IEEE Standard on Piezoelectricity, ANSI/IEEE, Std 176-1987
6. S. Emeterio, Ferroelectrics **293**, 237 (2003). doi:10.1080/00150190390238450
7. X.H. Du, Q.M. Wang, K. Uchino, IEEE Trans Ultrason. Ferroelectr Freq Control **50**, 312 (2003). doi:10.1109/TUFFC.2003.1193625
8. S. Zhang, J. Luo, W. Hackenberger, T.R. Shrout, J Appl Phys **104**, 064106 (2008). doi:10.1063/1.2978333
9. S. Zhang, C.A. Randall, T.R. Shrout, Solid State Commun **131**, 41 (2004). doi:10.1016/j.ssc.2004.04.016
10. S. Zhang, S. Lee, D. Kim, H. Lee, T.R. Shrout, J Am Ceram Soc **90**, 3859 (2007)
11. M.J. Haun, E. Furman, S.J. Jang, L.E. Cross, Ferroelectrics **99**, 80 (1989)
12. D. Damjanovic, j. Am Ceram Soc **88**(10), 2663 (2005). doi:10.1111/j.1551-2916.2005.00671.x
13. D. Damjanovic, Rep Prog Phys **61**, 1267 (1998). doi:10.1088/0034-4885/61/9/002
14. F. Li, Z. Xu, X. Wei, X. Yao, L. Jin, Appl Phys Lett **93**, 192904 (2008). doi:10.1063/1.3025842
15. D. Damjanovic, J Appl Phys **82**, 1788 (1997). doi:10.1063/1.365981