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Determination of temperature dependence of piezoelectric coefficients matrix of lead zirconate titanate ceramics by quasi-static and resonance method

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Abstract

The piezoelectric coefficients (d_{33}, $-d_{31}$, d_{15}, g_{33}, $-g_{31}$, g_{15}) of soft and hard lead zirconate titanate ceramics were measured by the quasi-static and resonance methods, at temperatures from 20 to 300 °C. The results showed that the piezoelectric coefficients d_{33}, $-d_{31}$ and d_{15} obtained by these two methods increased with increasing temperature for both hard and soft PZT ceramics, while the piezoelectric coefficients g_{33}, $-g_{31}$ and g_{15} decreased with increasing temperature for both hard and soft PZT ceramics. In this paper, the observed results were also discussed in terms of intrinsic and extrinsic contributions to piezoelectric response.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Lead zirconate titanate (PZT) ceramics are considered one of the most important lead-based piezoelectric ceramics due to their excellent piezoelectric performance. These ceramics have been widely used for sonar, hydrophones, ultrasound generators, high-voltage generators, micropositioners, etc [1]. At present many electromechanical devices are used over a wide temperature range, such as underwater devices (0–100 °C) and transducers for well logging (high temperature). Therefore it is necessary to characterize the temperature behaviour of these ceramics in a wide temperature range. In recent years, a number of investigations have been carried out on determination of the temperature behaviours of PZT ceramics and other related piezoelectric materials [2–5]. However, in those reports the temperature dependence of piezoelectric coefficients was determined only by the resonance method at high frequency (i.e. resonance frequency). The temperature dependence of piezoelectric properties at low frequency, which is also important for some piezoelectric applications, is usually not included.

In this study, the quasi-static (Berlincourt-type) method will be introduced to determine piezoelectric coefficients d_{33}, $-d_{31}$, d_{15}, g_{33}, $-g_{31}$ and g_{15} of PZT ceramics under a temperature range of 20–300 °C at low frequency. In addition, the resonance method will also be used to study the temperature dependence of the piezoelectric coefficients matrix at high frequency, in order to compare with the corresponding dependence at low frequency.

2. Experimental theory

2.1. Berlincourt-type method

The direct piezoelectric coefficient can be measured by the following equation:

$$D_i = d_{ijk}\sigma_{jk}, \qquad (1)$$

where D_i is the generated piezoelectric charge, σ_{jk} is the applied stress. To determine piezoelectric coefficient d_{ijk}, the generated piezoelectric charge D_i must be measured as external stress σ_{jk} is applied to the sample.

For poled ceramics, there are three different piezoelectric coefficients that need to be measured because the poled ceramics have a C_{∞}/C_{6v} symmetry. The piezoelectric

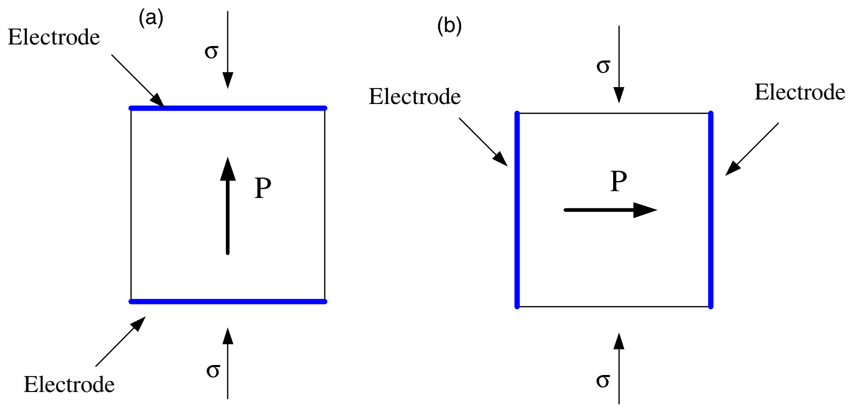

Figure 1. Schematic diagram of the direct piezoelectric measurements in (*a*) longitudinal mode for d_{33} and (*b*) transverse mode for d_{31}.

coefficients d_{31} and d_{33} can be conveniently obtained from the transverse and longitudinal modes, as shown in figures 1(*a*) and (*b*). On the other hand, the coefficient d_{15} cannot be directly measured by the Berlincourt-type method, since it is difficult to apply a shear stress (σ_5) to the sample. In this investigation we adopt another idea in order to avoid applying shear stress. Through the transformation rule of stress [6, 7], we know that the shear stress (σ_5) can be transformed into a tension and a compressive stress by a clockwise rotation of 45° about Z_2-axis. Therefore, in order to determine piezoelectric coefficient d_{15}, the sample is first poled along direction 3 and then cut along the plane (1 0 1) and (1 0 $\bar{1}$), as shown in figure 2. Consequently the coefficient d_{15} (in the original coordinate system) can be calculated with respect to d'_{31} and d'_{33} (in the new coordinate system), as depicted in figure 3.

2.2. Resonance method

For the resonance method, the value of the piezoelectric coefficient can be obtained through a specimen with suitable dimensions and poling direction [8]. These measurements basically consist of determining the electrical impedance of the vibrator as a function of frequency. The resonance, antiresonance frequencies and dielectric constant ε^{T} must be determined for calculating the piezoelectric coefficient. The details of this method are described in [8]. Note that the results calculated according to the IEEE standard are accurate only if the mechanical loss of the piezoelectric vibrator is small [9, 10], which means that the maximum phase angle of the vibrator should approach 90°.

3. Experimental procedure

3.1. Sample preparation

The commercial hard and soft PZT ceramics (PZT5 and PZT8) used in this study were obtained from BaoDing HongSheng Acoustics Electron Apparatus Co., Ltd [11]. The composition of these commercial ceramics is around the morphotropic phase boundary (between the tetragonal and the rhombohedral regions, at $x = 0.48$ in $PbZr_{1-x}Ti_xO_3$). The Curie temperature of the PZT5 [with donor dopants Sb^{5+} on (Zr, Ti) sites] and

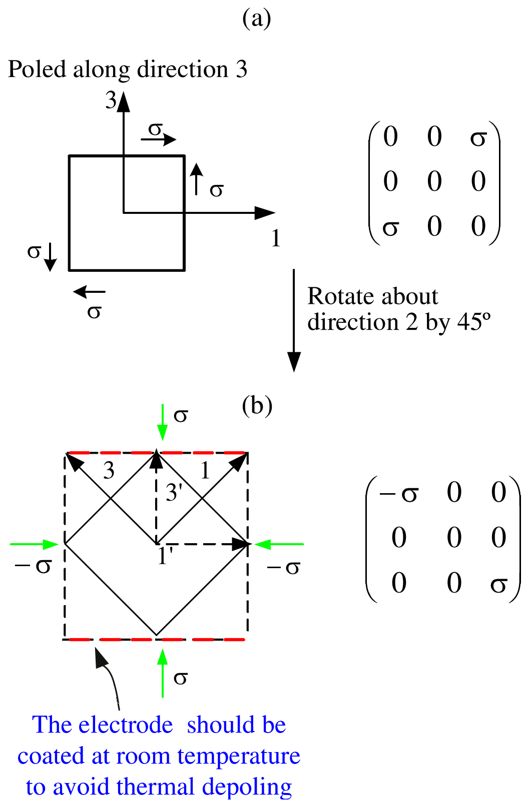

Figure 2. The principle diagram of a shear stress in the original coordinate system being transformed into two normal stresses in the new coordinate system. Also shown is the method of preparing the sample for testing d_{15}.

PZT8 ceramics (with acceptor dopants Fe^{3+} on (Zr, Ti) sites) are about 260 °C and 280 °C, respectively.

The ceramic samples with dimensions 6 mm × 6 mm × 6 mm were prepared as discussed in section 2.1, for the Berlincour-type measurements. The aspect ratio of these samples is larger than 1 : 2, so the lateral clamping effect can be eliminated [12, 13]. On the other hand, for the resonance techniques, the PZT samples were prepared with dimensions 20 mm × 3 mm × 0.6 mm (poled) for the length extensional mode of long thin plates (d_{31}), 6–8 mm (poled) × 1.5 mm × 1.5 mm for the length extensional mode of long thin rods (d_{33}) and 10 mm (poled) × 5 mm × 0.5 mm for the thickness

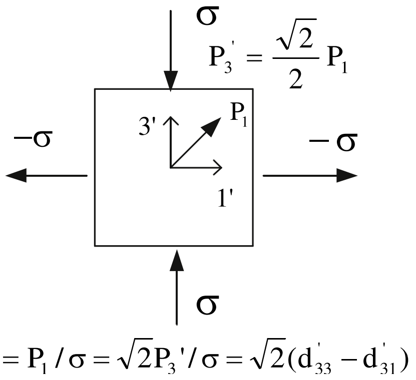

Figure 3. Schematic diagram of determination of the piezoelectric constant d_{15} by the quasi-static method.

shear mode (d_{15}). These dimensions, which would be used for calculating the corresponding piezoelectric coefficients, were recognized as invariant on the whole temperature range.

In this study the specimens used for determining coefficients d_{31} and d_{33} were first cut and then poled at 150 °C and a 30 kV cm^{-1} electric field. To determine d_{15}, the PZT ceramics were poled and then cut for Berlincourt-type and resonance measurements. Therefore, two specimens with the same dimensions (6 mm × 6 mm × 6 mm) were prepared, to investigate the effect of the cutting process on the piezoelectric behaviour of the PZT samples. The first one (named as S1) was cut at 0° from a poled sample and the second one (named as S2) was poled again after the cutting process.

3.2. Experimental equipment

Figure 4 shows the experimental setup for determining the temperature dependent piezoelectric coefficients by the Berlincourt-type method. In order to draw all piezoelectric-induced charge from the sample, the capacitance of the sample (C_s) and resistance R_1 should satisfy the relation: $1/\omega R_1 \gg C_s$ [8]. For the longitudinal mode, when an alternative force $F_3 = F_0 e^{i\omega t}$ is applied to the sample, the voltage through R_1 can be written as

$$V = I_1 R_1 = \frac{dQ}{dt} R_1 = \frac{d(F_0 e^{i\omega t} d_{33})}{dt} R_1 = j\omega R_1 F_0 d_{33} e^{i\omega t}, \tag{2}$$

where ω (about $2\pi \times 110$ in our measurement) and F_0 (about 0.5 N) are the angle frequency and amplitude of applied alternative force, respectively. d_{33} is the piezoelectric coefficient, t is the time. In this experimental system the voltage V was measured by a Lock-in amplifier (SRS830, Stanford research system). By the same means, the piezoelectric coefficient d_{31} was measured through the transverse mode.

To determine the temperature dependence of the piezoelectric coefficients by the resonance method, an impedance analyzer (HP-4294A, Hewlett-Packard) was used to measure the impedance spectrum of the 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 the sample holder.

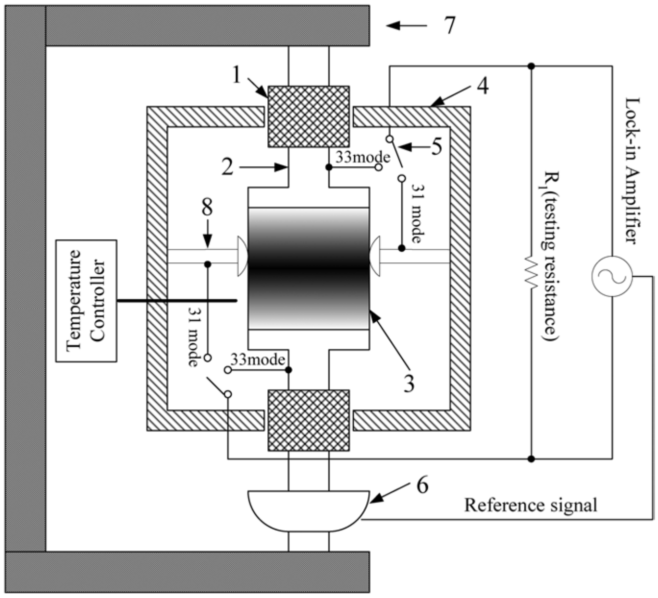

Figure 4. Experimental setup for measuring the temperature dependence of piezoelectric coefficients by the quasi-static method. (1) The mechanical contact for thermal and electrical insulation; (2) mechanical contact, which is an electrical conductor for longitudinal mode, or an electrical insulator for transverse mode; (3) PZT sample, which is cut with dimensions 6 mm × 6 mm × 6 mm for matching the mechanical contact; (4) furnace; (5) the double-throw switch, in order to measure the piezoelectric coefficient d_{33} or d_{31}; (6) ZJ-27 d_{33}-meter for applying alternative stress; (7) rigid frame; (8) electric contact for transverse mode.

4. Results and discussion

To investigate the effect of the cutting process on piezoelectric behaviour, the piezoelectric coefficient d_{33} of S1 and S2 (introduced in section 3.1) is measured by the Berlincourt-type method. For PZT5, the coefficient d_{33} of S1 and S2 are about 380 and 390 pC N^{-1}, respectively; for PZT8, the coefficient d_{33} of S1 and S2 are about 186 and 192 pC N^{-1}. The results indicate that the cutting process has little influence on the piezoelectric response of the PZT5 and PZT8 ceramics, which can be attributed to the quite high Curie temperature of the PZT5 and PZT8 ceramics.

Figure 5 shows the impedance and phase angle spectrum of the 33-mode PZT vibrators. It shows that the maximum phase angle approaches 90° even at rather high temperatures (for PZT5, the maximum phase is 83° at 250 °C; for PZT8, the maximum phase is 81° at 270 °C), which means that the effect of mechanical loss could be ignored and the calculated results are accurate upon the whole temperature range. Note that the resonant and the antiresonant peak will vanish as the temperature is higher than Curie temperature, as shown in figure 5. For the Berlincourt-type measurements, taking the determination of coefficient d_{33} as an example, figure 6 shows the measured voltage data, by which piezoelectric coefficient d_{33} can be calculated from equation (2). It can also be seen that the phase angle of voltage approaches 90° at temperatures below T_c, meaning that the imaginary part of the piezoelectric coefficient is rather small. In this investigation, we focus only on the real part of the piezoelectric coefficient.

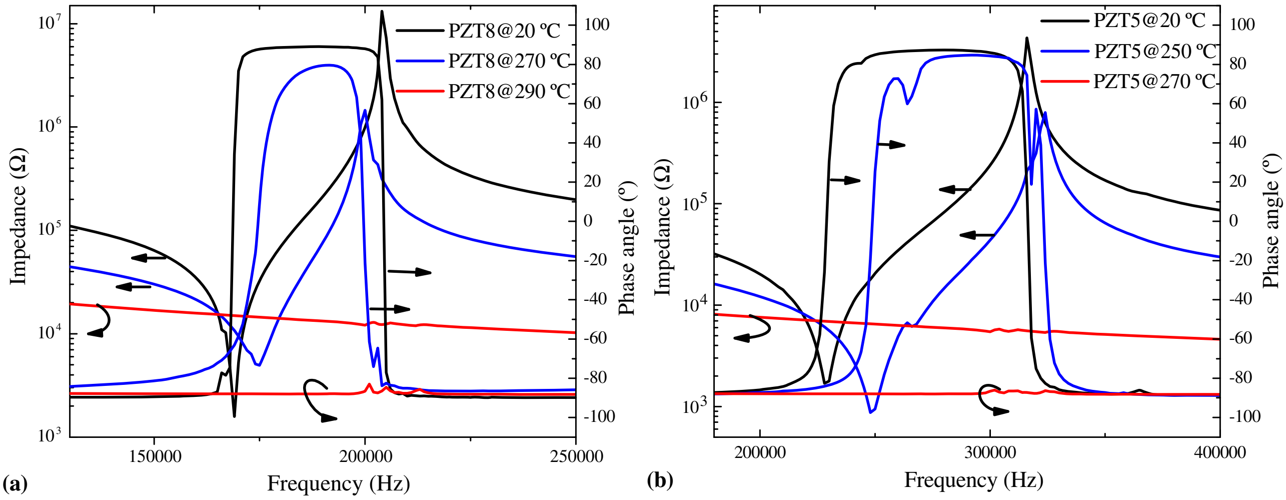

Figure 5. The impedance and phase angle spectrum of the 33-mode for (*a*) PZT8 and (*b*) PZT5.

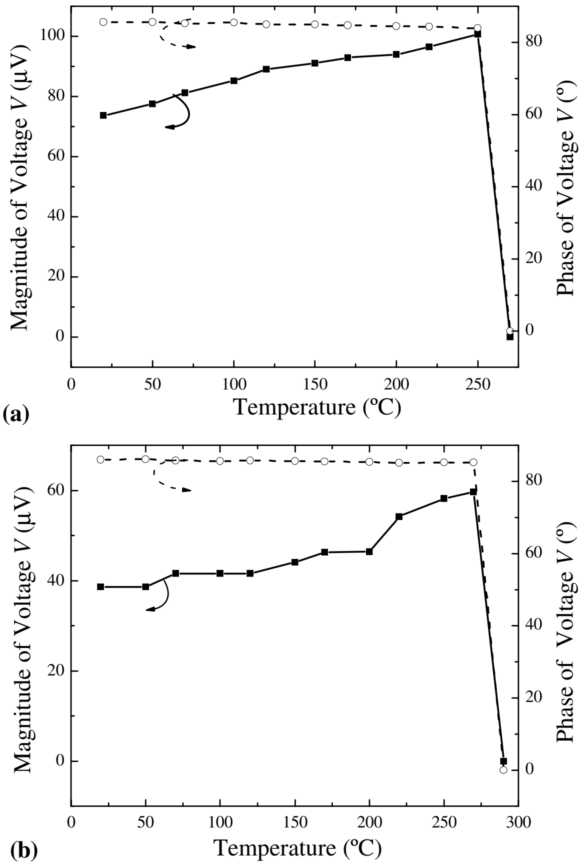

Figure 6. Data of the voltage through R_1 in quasi-static measurement for determining the temperature dependent-piezoelectric coefficient d_{33}. (*a*) PZT5 ceramics; (*b*) PZT8 ceramics.

Shown in figure 7 are the results of the temperature dependence of the piezoelectric matrix (*d* coefficient) for PZT5 and PZT8 ceramics. In order to exclude the randomness, these experiments are repeated three times and similar results are obtained. It is observed that the variation tendencies of the piezoelectric coefficients at low frequency are similar to those at the resonance frequency. The piezoelectric coefficients d_{33}, $-d_{31}$ and d_{15} of both PZT8 and PZT5 ceramics are found to increase with increasing temperature and reach maxima at phase transition temperature, and finally drastically fall to zero when the temperature is above Curie temperature (T_c). These results are similar to the reported results of PZT ceramics [2] at temperatures from 20 to 200 °C. Moreover, the piezoelectric response of other Pb-based ferroelectric materials also showed such an increasing tendency with respect to the temperatures below phase transition temperature [3–5].

As the temperature increases, the enhancement of coefficients *d* for PZT ceramics can be attributed to the following two mechanisms: (1) the extrinsic piezoelectric response (i.e. domain movement or switching [14, 15]) will be enhanced, because the thermal energy of the domains decreases and lower activation energy is required to make the domains change from one minima state to another; (2) the piezoelectric response of PZT in the single domain state will also increase with increasing temperature, as calculated in [16]. Although the data of PZT single domain have not been reported, the increase in piezoelectric response in the single domain state with increasing temperature was evidenced by some experiments on other Pb-based piezoelectric single crystals [3–5]. For example, the coefficient d_{33} of (0 0 1) oriented BS-PT single domain with tetragonal symmetry was reported to increase with increasing temperature [4], and the coefficients *d* of (0 0 1) oriented PMN–PT, PMN–PIN–PT and PZT–PT single crystals with rhombohedral symmetry were reported to increase with increasing temperature below phase transition temperature $T_{R\text{–}T}$ [3, 5]. Where only four equivalent domain patterns exist [17], sequentially domain switching among these equivalent domains cannot contribute to piezoelectric response.

It is also seen in figure 7 that there are some differences between the level of piezoelectric coefficients measured by the quasi-static and resonance method, although the variation tendencies are similar. The reason for these differences can be summarized as follows: (1) the different experimental conditions, including the difference in the experimental frequencies, equipment and theories between these two measurements, as well as the difference in the peak stress levels in the vibrator and quasi-static sample; (2) the different states of

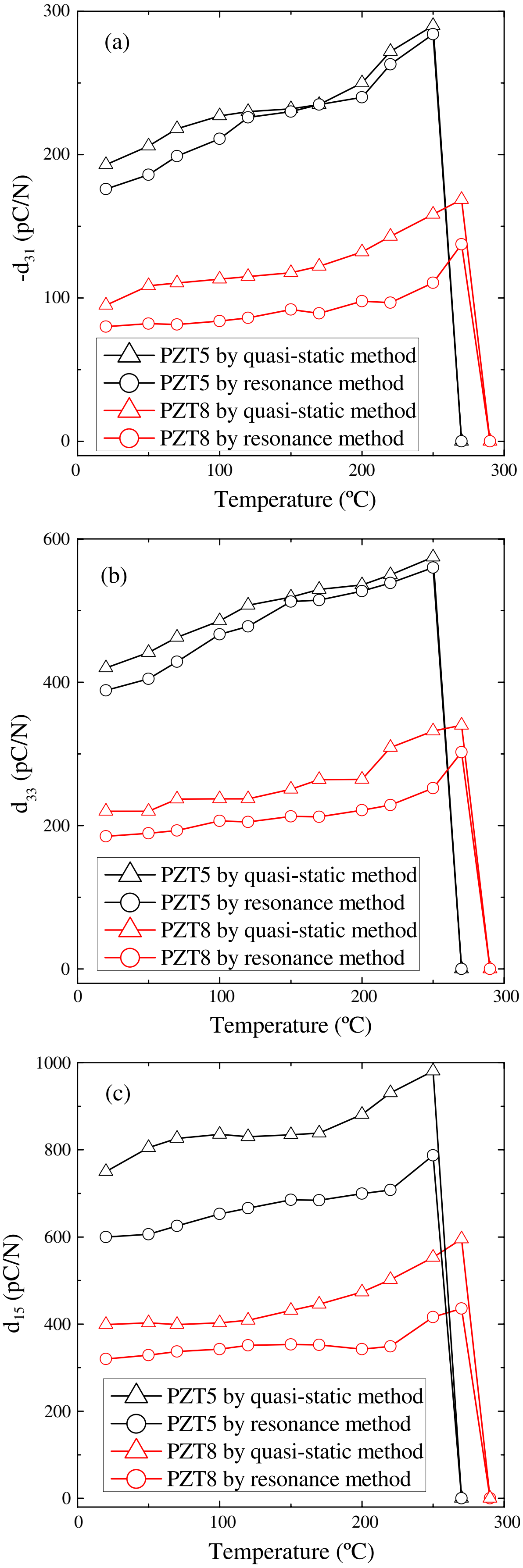

Figure 7. Temperature dependence of piezoelectric coefficients (*a*) $-d_{31}$, (*b*) d_{33}, and (*c*) d_{15} of PZT5 and PZT8 ceramics.

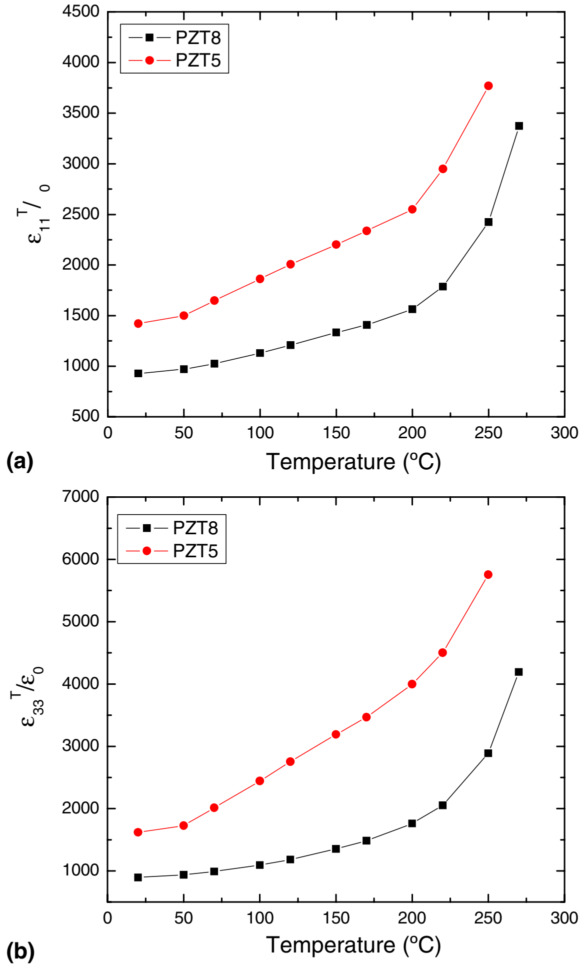

Figure 8. Temperature dependence of dielectric coefficients (*a*) ε_{11}^{T} and (*b*) ε_{33}^{T} for PZT5 and PZT8 ceramics, measured at 1 kHz.

specimens. The specimens with different dimensions are used to determine the piezoelectric coefficients in the quasi-static and resonance experiments, which could result in different degrees of poling for specimens because in the poling process the electric field fringe effects are different with respect to different aspect ratios.

Figure 8 shows the temperature dependence of 'free' dielectric constants of the PZT8 and PZT5 ceramics. Including dielectric constants and piezoelectric coefficients d, the temperature dependence of coefficients g_{33}, $-g_{31}$ and g_{15} are calculated ($g_{ij} = d_{ij}/\varepsilon_{ii}^{T}$), as presented in figure 9. The coefficients g_{33}, $-g_{31}$ and g_{15} of both PZT8 and PZT5 ceramics are found to decrease with increasing temperature and to be zero at Curie temperature. According to thermodynamic theory [18], it is suggested that the relationship between spontaneous polarization (P) and coefficient g is a direct ratio ($g \sim P \cdot Q$, where Q is the electrostrictive constant) and spontaneous polarization will decrease with increasing temperature for ferroelectrics. Thus, the decreasing tendency of coefficients g with respect to the temperature could be attributed to the decrease in spontaneous polarization with increasing temperature.

It should be noted that the frequency dispersion of ε^{T} is ignored in calculating coefficients g, because ε^{T} of

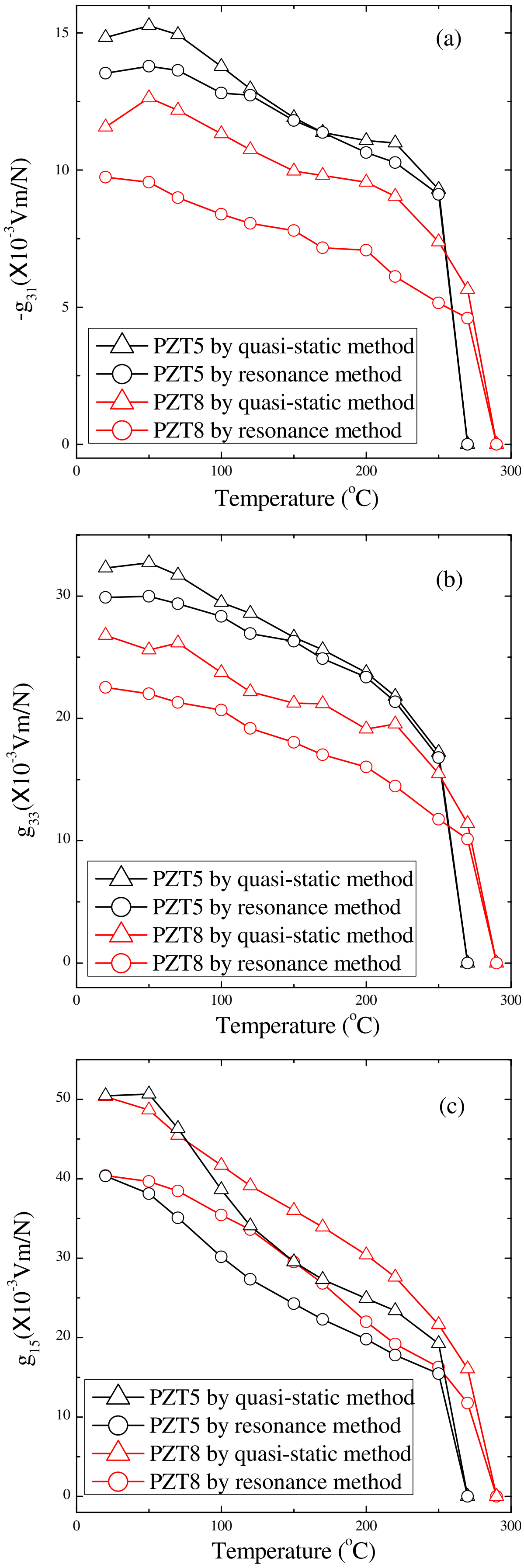

Figure 9. Temperature dependence of piezoelectric coefficients (*a*) $-g_{31}$, (*b*) g_{33}, and (*c*) g_{15} of PZT5 and PZT8 ceramics.

the poled PZT ceramics must be measured at frequencies substantially lower than the lowest resonance frequency, in which case the measurements yield the dielectric permittivities as constant stress [8]. 1 kHz is usually selected as the measurement frequency, because the lower frequency would reduce the experimental accuracy. Furthermore, we measured the frequency dependence of the dielectric constant for the unpoled PZT5 and PZT8 samples and found that the dielectric constant was independent with frequency from 1 kHz to 1 MHz, which suggests that the assumed absence of frequency dispersion in the dielectric and piezoelectric coefficient data is acceptable.

5. Conclusions

In this paper, the temperature dependence of the piezoelectric coefficients matrix for PZT ceramics was determined by the Berlincourt-type and resonance method. The results showed that the temperature dependence of the piezoelectric coefficients at low frequency was similar to that at resonance frequency. Moreover, it was also found that the temperature dependence of the piezoelectric response for hard PZT ceramics was similar to that for soft PZT ceramics. These results should provide a basis for future piezoelectric device design.

Acknowledgments

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